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Magnetic Exchange Coupling and Single-Molecule Magnetism in Uranium Complexes

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Magnetic Exchange Coupling and Single-Molecule Magnetism in Uranium Complexes

by

Jeffrey Dennis Rinehart

A dissertation submitted in partial satisfaction of the
requirements for the degree of
Doctor of Philosophy
in
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Graduate Division
of the
University of California, Berkeley

Committee in charge:

Professor Jeffrey R. Long, Chair
Professor Richard A. Andersen
Professor Michael F. Crommie

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Abstract

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by

Jeffrey Dennis Rinehart

Doctor of Philosophy in Chemistry

University of California, Berkeley

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This dissertation describes the research that led to the discovery of single-molecule magnetism in the actinides. Chapter One is an introduction to the concepts that lead to single-molecule magnet behavior with an emphasis on the specific qualities of the f-elements that make them interesting for such studies. A simple model for predicting ligand field environments that should be amenable to single-molecule magnet behavior is presented along with several examples of its application to lanthanide and actinide systems. The study of magnetic exchange coupling in uranium-containing multinuclear complexes is discussed and the literature on the subject is reviewed.

Chapter Two describes how the homoleptic dimer complex [U(Me2Pz)4]2 (Me2Pz– = 3,5-dimethylpyrazolate) can be cleaved via insertion of terminal chloride ligands, such that reactions with (cyclam)MCl2 (M = Ni, Cu, Zn; cyclam = 1,4,8,11-tetraazacyclotetradecane) in dichloromethane generate the linear, chloride-bridged clusters (cyclam)M[(μ-Cl)U(Me2Pz)4]2. Variable-temperature magnetic susceptibility is used to reveal the presence of weak ferromagnetic coupling between the Ni(II) (S = 1) and U(IV) centers and no coupling between the Cu(II) (S = 1/2) and U(IV) centers. Consistent with a simple superexchange mechanism for the coupling, density functional theory calculations performed on a [(Me2Pz)4UCl]− fragment of the cluster show the spin resides in 5f_{xyz} and 5f_{x^2-y^2} orbitals, exhibiting δ symmetry with respect to the U-Cl bond.

Chapter Three extends the analysis of exchange coupling in Chapter Two to include the (cyclam)Co[(μ-Cl)U(Me2Pz)4]2 cluster. As in the Cu(II) case, Co(II) has a single unpaired electron (S = 1/2), however this unpaired electron resides in a d_{z^2} orbital and is therefore oriented directly along the superexchange pathway. This provides a significantly better magnetic exchange pathway leading to the strongest magnetic coupling of the series.

Chapter Four deviates briefly from the pursuit of molecular magnets to study a series of multinuclear clusters formed from the activation of the 3,5-dimethylpyrazolate anion by uranium(III) via two-electron reductive cleavage of the N–N bond to form 4-ketimidopent-2-ene-2-imido (kipi3–) units, as isolated in three related tetranuclear uranium cluster compounds, two of which are mixed valent. The kipi3– ligand represents an exotic latecomer to the acetylacetonato
(acac\textsuperscript{−}) ligand family. Unlike the related and widely-utilized β-diketimido (nacnac\textsuperscript{−}) ligands, kipi\textsuperscript{3−} can be represented as containing both imido and ketimido functionalities. Thus, it provides a true nitrogen-based, isoelectronic analogue of acac\textsuperscript{−}, a ligand that has played a long and vital role in coordination chemistry.

Chapter Five turns from the synthesis of exchange coupled clusters to mononuclear species. Drawing on the model of f-element anisotropy presented in Chapter One, the trigonal prismatic complex U(Ph\textsubscript{2}BPz\textsubscript{2})\textsubscript{3} was chosen for study. Ac magnetic susceptibility measurements performed on it demonstrate the presence of slow magnetic relaxation under zero applied dc field. Analysis of both the temperature and frequency dependence of the ac susceptibility indicate a temperature regime (T > ~3 K) where Arrhenius behavior dominates the relaxation processes, leading to a spin relaxation barrier of $U_{\text{eff}} = 20 \text{ cm}^{-1}$. The dc field dependence of the relaxation time is studied to reveal evidence of quantum tunneling processes occurring at lower temperatures. The results represent the first example of an actinide complex displaying single-molecule magnet behavior and confirm the general strategy for identifying further uranium(III)-based single-molecule magnets by concentrating ligand field contributions above and below the equatorial plane of an axially-symmetric coordination complex.

Chapter Six builds on the results presented in Chapter Five to characterize the related complex the trigonal prismatic complex U(H\textsubscript{2}BPz\textsubscript{2})\textsubscript{3}. This tricapped trigonal prismatic complex is characterized by single crystal x-ray diffraction and ac magnetic susceptibility measurements. The ac susceptibility data demonstrate the presence of multiple processes responsible for slow magnetic relaxation. Out-of-phase signals observed at ac switching frequencies between 1 and 1500 Hz in dc fields of 500-5000 Oe indicate a thermal relaxation barrier of ca. 8 cm\textsuperscript{−1} for the molecule, with a temperature-independent process taking over at the lowest temperatures probed. Significantly, an unprecedented, slower relaxation process becomes apparent for ac switching frequencies between 0.06 and 1 Hz, for which a monotonic increase of the relaxation time with applied dc field suggests a direct relaxation pathway.
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To my parents,

Dennis and Nancy Rinehart
I begin by acknowledging my advisor, Prof. Jeffrey Long, not simply because it is standard issue to do so, but because he truly is the single most important factor to which I can attribute any success I was able to achieve during my time at Berkeley. I am grateful both for his excellent guidance as well as his willingness to let me take my project in the directions I found most interesting.

As great of an advisor as he is, there are two people who have had to deal with me much longer than he has: my parents, Denny and Nancy Rinehart. Though I know they will be proud of me no matter what I accomplish in life, I hope that they can take some additional pride in knowing that this dissertation, though it may be boring and jargon-filled, is dedicated to them and all of the work that they have done to get me here. I also need to thank my older brother, Scott, whose relentless emotional, physical, and psychological abuse during our childhood prepared me so well for graduate school in the physical sciences.

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Having spent my entire graduate student career in the same three-room apartment, I’ve developed a great attachment to my temporary home, as well as the many people who have come and gone since I moved in. Dan Montiel has been a constant supplier of joy, terror, confusion, friendship and other similar emotions since we first met nearly ten years ago. Being roommates for seven of those years I’ve had the privilege of getting to know him as few do; we may actually qualify for common-law marriage, but I’m keeping my options open for now. Andrew and Steph Cramer have been great sources of support and encouragement, and they are also the only reason we have any decorations, dishes, or furniture in the apartment. Pete Hillman and Young Chang, even after moving out and becoming adults, have provided me with delicious meals and good company. Young remains the only person I know who can win a board game through sheer force of will (and threat of violence). More recently, I’ve had the pleasure of working and living with Brian Wiers and Xiaowen Feng. Brian’s immeasurable knowledge of science is only exceeded by his knowledge of everything else. A strict adherent to the laws of thermodynamics, any order he creates in the chemistry lab is overwhelmed by the chaos he inflicts nightly upon our kitchen. Mr. Xiaowen “Spanky” Feng is the newest occupant of the apartment and lends it a distinct international flavor. His enthusiasm for discussing his chemistry is relentless, and many times I’ve been able to trade a bit of chemistry knowledge for a plate of his specialty: pan-fried chicken hearts with fennel.

A careful historian of 3001 Ellis St. Apt C may note that I’ve failed to mention a prominent West Virginian tenant: Dr. T. David Harris. Dave goes in a separate category because he fits in too many categories. He is a friend, coworker, confidant, motivator, and a million other things. Dave does everything, especially chemistry, with more heart than anyone I’ve ever met. The discussions we had about life and chemistry (including a few eight hour “working” lunches) will aid me for the rest of my life.
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Though the f-element project remains a small part of the Long Group, it could not succeed without the help of those on different (and often more easily fundable) projects. Since I have started, dozens of people have passed through the lab, and I have benefitted from both their expertise and their camaraderie. When I started, Eric Welch was a great help to me, teaching much of the solid state chemistry I hope to never have to use again. Louise Berben and Lianne Beltran were also instrumental in welcoming me to the lab. Steven Kaye was a great help to me offering strategic approaches to both my chemistry and the logistics of fighting various primates trained in the deadly art of karate. Hemamala Karunadasa was both there to help me when I started, and as I finish (due to a postdoc that allowed her to retain the same desk). Her fierce protectiveness of the glovebox and impossibly dry sense of humor contributed equally to my graduate experience. Joe Zadrozny has been a great addition to the lab. His easy-going humble nature belies an intelligence and commitment to success that not many have. His sense of humor, though frequently transcending my comprehension, will be sorely missed when I leave. Kenji Sumida, conqueror of beryllium and tamer of the robot, can make even the most boring and tedious events exciting with his baseball commentator voice. Charlene Tsay remains the kindest and most level-headed person I know. Without her anxiety-reducing influence, I most likely would have far less than the eight knuckles I have today.

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Several visiting professors were also important to my time here, especially two South Africans: Delia Haynes and Jeremy Smith. I learned the intricacies of the South African accent from Delia, and also that one can be a professor and still be cool. Jeremy was equally responsible for expanding my knowledge of carbene chemistry and of films that I will never be able to forget, no matter how hard I try.

Many post-docs have passed through the lab too and left their mark. Bart Bartlett helped me to get started in magnetism and proved that no matter what compromising photos of you exist, you can still get a great job in chemistry. Marty offered not only his help and advice, but also use of the Clubhouse beds after a long night at Beckett’s followed by Taco Bell. Though I prefer to avoid organic synthesis like the plague, Leslie Murray is the only reason I know how to do any (no mean feat). Also, his computer knowledge prevented me from taking a baseball bat to the lab printer on multiple occasions. Muralee Murugesu was a great help not only when in the Long group, but also now as a professor. His dysprosium work continues to change the direction of the field of single-molecule magnetism. Hye Jin Choi is the person I could always go to when I had a molecular magnetism question that nobody has the least idea about. Her knowledge is vast and all the more valuable for her generous and good natured willingness to share it.

I’m also indebted to a number of international students, post-docs, and visiting scholars. Winking Huang was my first introduction to Chinese culture. His friendship and sense of humor have been important to me both in lab and when I got the chance to visit him in Guangzhou. Kentaro Tamaki taught me how to run a column and also taught me the meaning of a number of English words and phrases I was probably better off not knowing. Valentina Colombo was here only briefly, but her enthusiasm was contagious, and her parties at Keith House weren’t over until the police arrived or the furniture was broken.

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To anyone I may have left out: please do not be offended. Discretion dictates that I end this section before it exceeds the length of my actual dissertation.
Chapter 1: An Overview of the Relevance of f-elements to Single-Molecule Magnet Research

1.1 Single-Molecule Magnetism in the Transition Elements

The story of single-molecule magnetism (and every presentation, book, paper introduction, and dissertation on the subject) inevitably begins with the discovery that upon removal of an external magnetic field, a magnetic moment could be maintained in the molecule \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\), \(\text{Mn}_{12}\text{-OAc}\) (1.1, left). This demonstration of slow magnetic relaxation in a zero-dimensional material gave birth to the field of single-molecule magnetism, and the molecule \(\text{Mn}_{12}\text{-OAc}\) became the “drosophila” of the single-molecule magnet field, leading to hundreds of publications on its magnetic properties. This is due partially to it being the first such system discovered, and partially to its holding the record energy barrier to spin reversal for the majority of the lifetime of the field. However, its ubiquity may also be for pedagogical reasons, as its magnetic behavior can be easily described using a double well potential model (Figure 1.1, right). At low temperatures, its ring of eight \(\text{Mn(III)}\) ions antiferromagnetically coupled to four \(\text{Mn(IV)}\) ions yields a well isolated \(S = 10\) ground state. This well isolated, strongly coupled ground state forces the magnetic moment to behave as a collective unit or “giant spin.” An axial anisotropy induces a splitting of the \(2S + 1\)-fold degeneracy of this ground state.

**Figure 1.1.** Magnetic structure of the molecule \(\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4\), \(\text{Mn}_{12}\text{-OAc}\) (left) and representation of its low lying electronic structure (right). Orange arrows, green arrows, red spheres, and grey spheres represent \(\text{Mn(III)}\), \(\text{Mn(IV)}\), oxygen, and carbon respectively. The orientation of the arrows represents the antiferromagnetic coupling between \(\text{Mn(III)}\) and \(\text{Mn(IV)}\) ions leading to an overall \(S = 10\) ground state. A representation of the splitting of this \(S = 10\) ground state by the axial anisotropy term, \(D\), leads to a bistable ground state with \(m_S = +/- 10\).
state leading to an energy barrier to reversal of the spin. This double well model offers an iconic visual representation of the bistable ground state separated by an energy barrier to spin inversion. Using this model it is easy to visualize the mathematical relationship between the axial zero-field splitting term $D$ and the total spin, $S$, of the complex by the relation $U = S^2|D|$, where $U$ is the anisotropy barrier to reorientation of the spin from $m_S = 10$ to $m_S = -10$ states or vice versa. For the original Mn$_{12}$-OAc molecule this energy barrier was $44$ cm$^{-1}$. It can easily be seen that this value is significantly lower than the expected value of $S^2|D| = 52$ cm$^{-1}$, but the introduction of a rhombic anisotropy term solves this discrepancy by accounting for tunneling between $m_S$ states. It is important to note that even if Mn$_{12}$-OAc were to display its full relaxation barrier, magnetic hysteresis can only be observed at several Kelvin.

From the beginning of the field of single-molecule magnetism, an important goal for synthetic chemists has been to design molecules that have higher anisotropy barriers, thus allowing for functional molecular magnets in a more accessible temperature regime. Yet for over a decade, a simple derivative of Mn$_{12}$-OAc, Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Br)$_{16}$(H$_2$O)$_{4}$, held the record for the maximum anisotropy barrier with $U_{\text{eff}} = 52$ cm$^{-1}$. With such small progress in increasing the anisotropy barrier, the goal of magnetic memory devices at even liquid nitrogen temperature remains well out of reach (Figure 1.2). One reason for the lack of improvement is that a main synthetic focus has been to increase the spin, which, according to the model $U = S^2|D|$, have a

![Figure 1.2. Plot of the required anisotropy barrier for a single-molecule magnet with a relaxation time of 10 y (blue) and 1 s (red) at a given temperature. The value of $\tau_0$ is assumed to be $10^{-9}$ s. Dashed black lines mark the boiling temperature of liquid nitrogen (77 K) and 300 K with colored dashed lines marking the required anisotropy barrier for magnetic blocking at those temperatures. The purple rectangle represents the extent of current single-molecule magnet technology.](image)
drastic effect on the anisotropy barrier. However, this simple model fails to account for the interrelated nature of $S$ and $D$.\(^4\) Thus, the drastic increases in spin achieved by synthesizing larger multinuclear clusters (up to a record value of $S = 83/2$)\(^5\) have been accompanied by corresponding drop-offs in $D$. Therefore, the overall anisotropy barriers for such large spin compounds tend to be smaller than their lower spin counterparts. This lack of progress in raising the anisotropy barrier, one of the main aims of single-molecule magnetism, makes it imperative to explore radically different approaches to the problem.

1.2 The f-elements in Single-Molecule Magnetism

The introduction of the f-elements into single-molecule magnetism seems like one obvious approach, due to their large potential number of spins per ion, in addition to their high potential magnetic anisotropies. In fact, some of the strongest ferromagnets yet discovered (e.g. SmCo$_5$ and Nd$_2$Fe$_{14}$B) owe their magnetic properties largely to the influence of f-element anisotropy. Despite these advantages, lanthanides only started to appear in the single-molecule magnet literature in 2003, with the publication of Ishikawa’s work on [LnPc$_2$]$^n$ (Ln$^{III}$ = Tb, Dy, Ho; H$_2$Pc = phthalocyanine; $n = −1, 0, +1$).\(^6\) That work was treated with some suspicion due to the extremely high anisotropy barrier for [TbPc$_2$]$^−$ of 230 cm$^{-1}$, which was almost four times as high as the record holding molecule at the time, lack of hysteresis, and presence of only one magnetic ion. Due to this suspicion and radically different phenomenon leading to their single-molecule magnet behavior, very little work was done with the lanthanides, although in recent years that has begun to change (Figure 1.3). The actinides got an even later start in the field, with the first evidence of actinide single-molecule magnetism appearing in late 2009.\(^7\) Though f-elements have only started to gain momentum in the single-molecule magnet literature in the last few years, their magnetic properties have already surpassed transition metals by many figures of merit including hysteresis temperature and anisotropy barrier (Figure 1.4).

![Figure 1.3. Plot of publications related to f-element single-molecule magnetism by year.](image)
The f-elements’ late entrance into the field of single molecule magnetism may be a consequence of the early focus of the field on exchange coupled clusters. Due to the valence f-orbitals, the actinides and especially the lanthanides show relatively poor magnetic exchange. While generally true, the limitations and consequences of this statement will be addressed further in Section 1.5 and in chapters 2 & 3. In any case, the reason the f-elements were finally utilized and have been growing in prominence in the field is the powerful effects of single-ion (magnetocrystalline) anisotropy. A general discussion of this phenomenon and its application to single-molecule magnetism is given in the next section and specific examples of its employment are presented in chapters 5 & 6.

**Figure 1.4.** Plot of the highest recorded hysteresis temperature vs. the anisotropy barrier for select single-molecule magnets. Here, hysteresis is defined as showing a measurable coercive field in a plot of field vs. magnetization. Blue, teal, and green symbols represent transition metal-, actinide-, and lanthanide-based single-molecule magnets, respectively. Squares and circles represent single-ion and multinuclear clusters, respectively. The dotted line represents the theoretical highest hysteresis temperature that should be observed with $\tau_0 = 10^{-9}$ s and a minimum relaxation time of 1 s for observable hysteresis. Numbers indicate the reference from which the data were extracted as follows: 1 – U(Ph$_2$BPz$_2$)$_3$ (ref 7); 2 – [(PY5Me$_2$)$_4$Mn$_4$Re(CN)$_7$]$^{4+}$ (ref 8); 3 – [Dy$_4$(L)$_4$(MeOH)$_6$] (ref 9); 4 – [TbPc$_2$]$^-$ (ref 6a,b); 5 – [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Br)$_{16}$(H$_2$O)$_4$] (ref 10); 6 – Mn$_{12}$-OAc (ref 2); 7 – [{Pc(OEt)$_8$}$_2$Dy]$^+$ (ref 6c); 8 – [Mn$_6$O$_2$(sao)$_6$(O$_2$CPh)$_2$(EtOH)$_4$ (ref 11); 9 – [Co(hfip)$_2$(D$_2$py$_2$(TBA))]$_2$ (ref 12) 10 – [Dy$_4$(µ$_3$-OH)$_2$(bmh)$_2$(msh)$_4$Cl$_2$] (ref 13); 11 – {[(Me$_3$Si)$_2$N]$_2$(THF)Dy$_2$}(µ-η$_2$-η$_2$-N$_2$)[K-18-crown-6] (ref 14).
Figure 1.5. Schematic representation of the electronic structure of an ion with a [Rn]5f$^2$ electronic configuration such as U(IV). The crystal field ($m_J$) states are represented as a box because the actual splitting of the $2J + 1 = 9$ states can vary significantly with the symmetry and strength of the ligand field. Although the diagram is qualitative, the crystal field splitting is usually between 100 – 2000 cm$^{-1}$. This is similar enough to the spin-orbit coupling energy to lead to significant mixing of states.
1.3 Complexity of the f-element Electronic Structure

While strong single-ion anisotropy makes the f-elements enticing targets for single-molecule magnet research, it also leads to extremely complex electronic structure. This means that the majority of the simplifications and assumptions made for transition metal chemistry lead to gross inaccuracies when applied to f-elements.

In the molecular chemistry of first-row transition metal ions, it is usually possible to treat the magnetic susceptibility as being solely due to the unpaired spins, with only perturbational effects from the orbital components owing to an orbital angular momentum that is largely quenched by the ligand field. The “spin-only” approximation, which works reasonably well for most first-row transition metal species, loses its validity for a number of molecular systems of interest for magnetism, including those containing actinide ions. For example, a UIV center possesses two unpaired 5f electrons, leading to a 3H(S = 1, L = 5) ground state. Spin-orbit coupling produces an energy splitting based on the total angular momentum, J, where |S − L| ≤ J ≤ L + S. For the UIV ion, which has a less than half filled 5f shell, this leads to a 3H4(J = 4) designation for the spin-orbit coupled ground state (Figure 1.5). Depending on the degree of spin-orbit coupling, mixing with excited state Russell-Saunders terms of the same J value can occur. Recent calculations on the UIV ion suggest that the 3H4 ground state can have significant 1G4 character (9% in the case studied). This mixing of excited state Russell-Saunders terms into the ground state invalidates S and L as individual quantum numbers and can also restore orbital angular momentum by mixing other f orbitals into the ground state wavefunction.

The discussion thus far has neglected the effects of the ligand field, which turns out to be the key factor in making f-elements interesting for single-molecule magnetism. It is this interaction between the ground spin-orbit coupled J state and the ligand field which creates the magnetic anisotropy barrier separating opposite orientations of the spin ground state. The ligand field perturbation removes the (2J + 1)-fold degeneracy of the ground state. The degeneracy of these mJ sublevels is determined by symmetry, and their energies are subtly affected by the orientation and strength of the ligand field. This splitting of nearly-degenerate mJ states is nearly impossible to predict quantitatively and extremely time consuming to determine empirically. Several empirical methodologies have been employed but they will not be discussed in detail here. These methods include the simultaneous least squares fitting of paramagnetic nmr shifts and magnetic susceptibility, low temperature spectroscopic analysis of high symmetry single crystals, and computational fitting of magnetic susceptibility data to a Hamiltonian with terms accounting for interelectronic repulsion, spin-orbit coupling, ligand field effect, isotropic exchange interactions, and applied magnetic field. These methods are all able to characterize compounds that have shown interesting behavior but are unable to predict which molecules will have the requisite electronic structure for showing single-molecule magnetic behavior. Thus a
simple, predictive method for determining the approximate ordering of the $m_J$ states of the ground spin-orbit-coupled term is necessary for rationally designing f-element single-molecule magnets. Such a model has long been used to explain single-ion anisotropy, however its specific application to the design of single-molecule magnets has not been detailed. Below is an outline of the model with specific, illustrative examples of its implementation.

1.4 Exploiting Single-ion Anisotropy in the Design of f-element Single-molecule Magnets

Single-ion (or magnetocrystalline) anisotropy is caused by the interaction between spin-orbit coupled electrons with a non-spherical crystal field environment. The high orbital angular momentum and near degeneracy of the f-orbitals promotes coupling between the orbital motion of the electrons and their intrinsic spin. This spin-orbit coupling forms an indirect pathway whereby the spin can interact with the crystal field environment. This means that, with an understanding of the shape of the f-electron density for a given state, we can predict whether that state will have a high or low energy in a given crystal field environment. Thus, the splitting of the $2J + 1$-fold $m_J$ states composing the low-lying electronic structure can be qualitatively ordered. Since current models of paramagnetic relaxation hold that the thermally activated process leading to slow magnetic relaxation involves only the ground state and first excited state, this rudimentary knowledge should be enough to predict those molecules that will be good single-molecule magnets and those that will not.

Put another way, we hope to satisfy two conditions to design good f-element single-molecule magnets: First, the highest magnitude $\pm m_J$ state should form a doubly-degenerate ground state. This ensures that we will have a high magnetic moment at temperatures where only the ground state is significantly populated and also limits the rate of quantum tunneling because as the magnitude of the angular momentum change between tunneling states increases, the tunneling rate should decrease. Second, there should be a large separation between that ground state and the first excited state. If these two conditions are satisfied, we should maintain a magnetic ground state and severely slow the magnetic relaxation at temperatures below the ground state to first excited state gap. This scenario leaves us with two general cases based on the basic overall shape of the f-electron density. This shape is simply determined by the Hund’s
rules ground state of the ion and will be invariant for a particular lanthanide in a particular oxidation state. It is described by the quadrupole moment of the f-electron charge cloud which is either prolate (axially elongated), or oblate (equatorially elongated). The isotropic (spherical) case is uninteresting for single-molecule magnets due to its lack of anisotropy. The quadrupole moment distributions of the lanthanides are shown in Figure 1.6. From Figure 1.6 it is evident that a given crystal field environment will have a very different effect on the electronic structure of oblate ions such as Ce(III), Pr(III), Nd(III), Tb(III), Dy(III), and Ho(III)) than it will on prolate ions such as Pm(III), Sm(III), Er(III), Tm(III), and Yb(III)). To maximize the anisotropy of an oblate ion, we should place it in an axial sandwich-type geometry with ligand electron density above and below the equatorially located f-element electron density (Figure 1.7). Conversely, for a prolate ion, an equatorially-coordinating geometry is preferable so as to minimize charge contact with the axially-located f-element electron density (Figure 1.8).

This very simple model offers a surprising amount of information about how to approach single-molecule magnet design for the f-elements. First of all, it explains why the majority of systems studied thus far have involved axially-coordinated ligand environments (because the most used ion, Dy(III), has an oblate electron density). In fact, Dy(III) may represent the ideal ion for single-molecule magnetism: it is a Kramers ion,\textsuperscript{16} so a doubly degenerate \( m_J \) ground state is ensured and it combines a large-moment \( ^6H_{15/2} \) ground state\textsuperscript{25} with significant anisotropy of the 4f shell. Tb(III) offers similar properties with an even greater electronic anisotropy, however a bistable ground state requires that rigorous axial symmetry be maintained since bistability is not guaranteed for a non-Kramers ion. This model also suggests a completely unexplored method of single-molecule magnet synthesis wherein an equatorial ligand coordination environment is coupled with an ion of prolate electron density as in Figure 1.8.

\subsection{1.4.1 Lanthanide Bisphthalocyanines}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.7}
\caption{Low (left) and high (right) energy configurations of the f-orbital electron density with respect to the crystal field environment for a 4f ion with oblate-type electron density (e.g. Ce(III), Pr(III), Nd(III), Tb(III), Dy(III), Ho(III)). The green arrow represents the orientation of the spin angular momentum coupled to the orbital moment. This particular combination of oblate electron density and “sandwich” crystal field minimizes the energy of the \( m_J = J \) (high spin) state, making it a desirable target for single-molecule magnet design.}
\end{figure}
As discussed above, the series of molecular magnets $[\text{LnPc}_2]^n$ ($\text{Ln}^{\text{III}} = \text{Tb, Dy, Ho}; \text{H}_2\text{Pc} = \text{phthalocyanine}; n = -1, 0, +1$) were the first lanthanide complexes to be identified as such. The anisotropy barrier measured for Tb$[\text{LnPc}_2]^-$ and its derivative compounds remains the highest for any system by nearly a factor of two. Its low-lying electronic structure was determined by the simultaneous least squares fitting of paramagnetic nmr shifts and magnetic susceptibility as described in reference 19. The energy splitting of the states for all of

![Figure 1.8](image1.png)

**Figure 1.8.** Low (left) and high (right) energy configurations of the f-orbital electron density with respect to the crystal field environment for a 4f ion with prolate-type electron density (e.g. Pm(III), Sm(III), Er(III), Tm(III), Yb(III)). The green arrow represents the orientation of the spin angular momentum coupled to the orbital moment. This particular combination of prolate electron density and “equatorial” crystal field minimizes the energy of the $m_J = J$ state, making it a desirable target for single-molecule magnet design.

As discussed above, the series of molecular magnets $[\text{LnPc}_2]^n$ ($\text{Ln}^{\text{III}} = \text{Tb, Dy, Ho}; \text{H}_2\text{Pc} = \text{phthalocyanine}; n = -1, 0, +1$) were the first lanthanide complexes to be identified as such. The anisotropy barrier measured for Tb$[\text{LnPc}_2]^-$ and its derivative compounds remains the highest for any system by nearly a factor of two. Its low-lying electronic structure was determined by the simultaneous least squares fitting of paramagnetic nmr shifts and magnetic susceptibility as described in reference 19. The energy splitting of the states for all of

![Figure 1.9](image2.png)

**Figure 1.9.** Structure of $[\text{TbPc}_2]^-$ ($\text{Pc}^2- = \text{phthalocyanine}$) shown perpendicular (left) and parallel (right) to the 4-fold axis. Green-blue, blue, and gray spheres represent terbium, nitrogen, and carbon respectively. Hydrogen atoms have been removed for clarity.
the latter paramagnetic lanthanides is given in Figure 1.10. From the model developed so far involving the quadrupole moment charge densities, it is easy to see that as the 4f density changes from highly oblate to highly prolate as the latter half of the 4f series is traversed, the ground state changes from relatively high \( m_J \) to relatively low \( m_J \) in the sandwich-type ligand environment of the \( \text{Pc}^{2-} \) ligands. This is simply a re-stating of the fact that Tb(III) and Dy(III) ions should be good single-molecule magnets in this type of environment. However, there are a number of interesting subtleties that require a more detailed version of the model, such as: Why is there such a noticeable separation between the ground state and first excited state for Tb[LnPc\(_2\)]\(^-\), and why is the electronic structure of Yb[LnPc\(_2\)]\(^-\) so seemingly random? These two questions cannot be explained by the model as presented so far, but if we include higher order terms in the multipole expansion of the f-electron density the reasons become clear. In the notation of Stevens, this means inclusion of \( \beta_J \) (or \( \theta_4 \)) = hexadecapole and \( \gamma_J \) (or \( \theta_6 \)) = hexacontatetrapole terms.\(^{26}\) These are included to give graphical representations of the angular dependence of the 4f charge density of the various \( m_J \) states composing the ground state \((2S + 1)_LJ\) term.\(^{27}\) For Tb(III) these free-ion charge densities are plotted in Figure 1.11. A cursory consideration of the anisotropy of these states reveals that the \( m_J = \pm 6 \) state has an extremely oblate electron density, making it ideal for the bis-phthalocyanine sandwich-type geometry. So upon insertion of the Tb(III) ion into the \([\text{TbPc}_2]^-\) crystal field, the \((2J + 1) = 13\)–fold degeneracy of the Hund’s rules \( ^7F_6 \) ground state is removed and the \( m_J = \pm 6 \) state lowers in energy to become the ground state. Conversely, the \( m_J = \pm 5, \pm 4, \pm 3, \pm 2, 0 \) states all have prolate electron densities making them extremely unfavorable for the sandwich-type geometry, leading to a rise in their energy with respect to the \( m_J = \pm 6 \) state. Thus the ground \( m_J \) state is \( \pm 6 \) and there is a large energy gap separating it from the \( \pm 5 \) state.

**Figure 1.10.** Splitting of the spin-orbit coupled \((J)\) ground state by a crystal field for \([\text{LnPc}_2]^-\) compounds as determined in reference 6b.
While most of the ions show some general progression from highest to lowest $m_J$ state or vice versa, ytterbium has a seemingly random energy splitting of the $m_J$ states. The angular dependence of the 4f charge density for the $m_J$ components of Yb(III) is plotted in Figure 1.12. Interestingly, the $m_J$ terms defy the general classification of “oblate” or “prolate” and take on a more varied angular dependence. However, once again the splitting shown in Figure 1.10 can be rationalized in terms of the interaction between the free ion charge densities and the ligand field. The $m_J = \pm 7/2$ has almost no oblate density, making it clearly the highest energy state, whereas the $m_J = \pm 5/2$ state is mostly composed of oblate density with only small lobes extending along the ±z direction. Considering that the Pc$^{2-}$ ligands have a central cavity along the z-axis, this should not create too much of an unfavorable interaction. However the $m_J = \pm 3/2$ and $\pm 1/2$ states have considerable prolate lobes that should form an intermediate interaction between the favorable one of $m_J = \pm 5/2$ and the extremely unfavorable one of $m_J = \pm 7/2$. Interestingly, these
charge densities also suggest that Yb(III) should form a highly favorable $m_J = \pm 7/2$ ground state in an axial coordination environment. Empirical electronic structure studies have shown this, but as of yet no single-molecule magnetism has been demonstrated.\textsuperscript{28}

### 1.4.2 SmCo\textsubscript{5}

While not a molecular species, it is interesting to apply the above model of anisotropy to a long-range ordering magnet that invokes lanthanide single-ion anisotropy to generate one of the strongest magnets known. Because the high coercive field of SmCo\textsubscript{5} is largely due to the magnetic anisotropy created by the delocalized band structure of cobalt interacting with the localized f-electrons on samarium, we can approximate its anisotropy in terms of a localized electronic model. SmCo\textsubscript{5} is composed of sheets of Sm(III) ions surrounded by six equatorially

![SmCo\textsubscript{5} Structure](image)

**Figure 1.13.** Representation of a layer of the SmCo\textsubscript{5} structure. Cobalt ions are represented as green spheres and samarium ions as prolate, purple ovoids.

![Charge Densities](image)

**Figure 1.14.** Charge densities of the $m_J$ components of the $^6H_{5/2}$ ground state of Sm(III).
coordinated cobalt ions as depicted in Figure 1.13. The prolate shape of the $m_J = \pm 5/2$ state (Figure 1.14) contrasts sharply with the oblate shapes of the $m_J = \pm 3/2$ and $\pm 1/2$ states, creating a highly anisotropic environment that is coupled to the delocalized cobalt moment thus anchoring the spins and resisting change in their orientation. It is interesting to note that all strong traditional magnets containing lanthanides incorporate the early lanthanides ($4f^n$, $n < 7$). This is because the $4f$ electrons of less than half filled f-shells will couple ferromagnetically to the delocalized transition metal electrons. This leads to a higher moment and stronger magnetism despite the lower overall moment contributed from the lanthanide ion. In single-molecule magnets, however, the late lanthanides can be used since magnetic coupling is either irrelevant (for mononuclear systems) or determined by the particular superexchange pathway present.

### 1.4.3 Plutonocene

All of the previous examples have focused on lanthanide systems. This is because the methodology presented here, namely that the ground spin-orbit coupled state can be considered well isolated and any mixing of states is negligible. This approximation tends to hold reasonably well since the generally weak interaction of the lanthanides with crystal field tends to be an order of magnitude smaller than the spin-orbit coupling interaction. Therefore, interactions between $m_J$ states are minimized and $m_J$ remains a fairly good quantum number to describe the system. Deviations from this are well known and account for many of the subtleties of lanthanide spectroscopy,\textsuperscript{16a} yet they go beyond the scope of the simple model presented here. Such deviations from state-mixing tend to be much more pronounced in the actinides, where much larger crystal field splittings are frequently observed. However, the model invoked above still

![Figure 1.15. Representation of the structure of Pu(COT)$_2$ (plutonocene, (COT)$_2^{-}$ = cyclooctatetraene). Purple, gray, and white spheres represent plutonium, carbon, and hydrogen respectively.](image)

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retains some predictive quality.

For example, the molecule Pu(COT)$_2$ (plutonocene; (COT)$_2^{-} =$ cyclooctatetraene dianion) (Figure 1.15) presents an interesting case since it shows only temperature independent paramagnetism despite having a non-diamagnetic $^5I_4$ ground state. By comparison with Pm(III) (Figure 1.6), Pu(IV) should have a prolate electron density ground state. In the sandwich-type crystal field environment of the (COT)$_2^{-}$ ligands, this should lead to a lowering of the energy of the $m_J = 0$ state which is diamagnetic. In agreement with this picture, the magnetic behavior observed for plutonocene is due to mixing between the non-magnetic ground state and low-lying excited states.

1.5 Magnetic Exchange-coupling in f-element systems

While the discussion thus far has centered on the single-ion properties of the f-elements, many promising single-molecule magnets of the transition elements have developed out of research on exchange coupled cluster compounds. Since exchange coupling in lanthanides has been reviewed extensively already, we will focus on the actinides here, specifically uranium.

It is commonly predicted that the actinides should show greater magnetic coupling due to the increased radial extension of the 5f compared to the 4f orbitals (Figure 1.16). This prediction arises from the fact that the superexchange mechanism common for magnetic coupling in molecular system can only function if there is orbital overlap between the spin-containing metal orbitals and the bridging ligand orbitals. Yet even with the growing number of varied synthetic systems incorporating paramagnetic uranium centers, unraveling actinide magnetic behavior remains a challenge. This is not due to the lack of a theoretical foundation as much as it is to the difficulty of separating the myriad interactions leading to the magnetic behavior of the f-elements. Accurately modeling the complex interactions governing the magnetic susceptibility of the actinides remains extremely unreliable in all but the simplest cases. The electronic complexity leads to a strong variation in the thermal population of the many states energetically comparable to the ground state. This effect becomes evident as the higher-energy $m_J$ sublevels depopulate as the temperature is lowered. Depopulation of these sublevels leads to a concommitant decrease in the magnitude of the total angular momentum vector. Two important

![Figure 1.16. Radial distribution functions for a [Xe]4f$^3$ (left) and a [Rn]5f$^3$ (right) electronic configuration.](image)
consequences arise from this phenomenon. First, the decrease in angular momentum manifests itself as a decrease in the magnetic susceptibility that can obscure other simultaneous effects, such as magnetic exchange coupling between bridged metal centers. Additionally, if such exchange coupling between the actinide ion and other metals in the cluster does exist, its magnitude will decrease, and in the case of low symmetry non-Kramers systems, eventually disappear at low temperature, as there is less angular momentum with which the spin of the non-actinide center can couple. Dealing with these single-ion effects, which obscure and interfere with the effects of magnetic coupling between metal centers, is of preeminent importance to the progression of the field of actinide molecular magnetism.

The following section contains a survey of recent developments in the synthesis and characterization of molecular systems in which actinide ions potentially engage in magnetic exchange interactions. Thus far, efforts have focused exclusively on species incorporating uranium, since this actinide element offers minimal radioactivity (in depleted form) with accessible oxidation states allowing for zero, one, two, or three unpaired electrons. Researchers have confronted the intricacies of the magnetic exchange in a number of interesting ways, often with the goal of identifying and, to the extent possible, quantifying ferro- or antiferromagnetic exchange coupling. Understanding these exchange interactions is not only essential to development of models for the basic electronic structure of the 5f elements, but also may represent the key to producing the first exchange coupled actinide-based single-molecule magnets.

1.5.1 A Diuranium Complex

The first observation of magnetic exchange coupling in an actinide-containing molecule was reported nearly twenty years ago for the binuclear, 1,4-dimidobenzene-bridged complex

![Figure 1.17](image-url)  

**Figure 1.17.** Experimental (symbols) versus calculated (lines) molar magnetic susceptibility for [(MeC₅H₄)₃U]₂(μ-1,4-N₂C₆H₄). Each calculated curve is modeled with a different amount of the paramagnetic impurity, (MeC₅H₄)₃U(thf). Taken from Ref 31.
The presence of coupling between the two U$^\text{V}$ centers within this molecule became evident upon comparison of its variable temperature magnetic susceptibility to that of structurally similar compounds. The geometric isomer [(MeC$_5$H$_4$)$_3$U]$_2$(µ-1,3-N$_2$C$_6$H$_4$), for instance, displays essentially constant magnetic susceptibility ($\chi_M$) with decreasing temperature from 300 K down to ca. 150 K, at which point it begins to rise monotonically as the temperature is decreased to 5 K. This behavior, typical of an isolated 5f$^1$ center, is essentially the sum of that observed for two (MeC$_5$H$_4$)$_3$U(NPh) complexes, and indicates the lack of any magnetic exchange between the two U$^\text{V}$ centers. In contrast, the magnetic susceptibility data obtained for [(MeC$_5$H$_4$)$_3$U]$_2$(µ-1,4-N$_2$C$_6$H$_4$) display similar behavior down to ca. 75 K, but then exhibit a downturn at lower temperatures, indicative of antiferromagnetic coupling (see Figure 1.17).

In an attempt to obtain a quantitative determination of the coupling in [(MeC$_5$H$_4$)$_3$U]$_2$(µ-1,4-N$_2$C$_6$H$_4$), the experimental $\chi_M$ vs. $T$ data were compared to calculated susceptibilities. The magnetic interaction between the U$^\text{V}$ centers was modeled employing the following Ising Hamiltonian for an isolated dinuclear complex:

$$H = -2J \hat{S}_{z1} \cdot \hat{S}_{z2} + g|| \mu_B \hat{H}_z (\hat{S}_{z1} + \hat{S}_{z2})$$

where $\hat{S}_{z}$ is the spin operator for each $S = \frac{1}{2}$ U$^\text{V}$ ion (the z direction is defined as along the U···U axis), $J$ is the exchange constant, $g||$ is the Landé g factor, $\mu_B$ is the Bohr magneton, and $\hat{H}_z$ is the magnetic field vector. Note that this Hamiltonian does not account for deviations in the magnetic susceptibility resulting from depopulation of the uranium excited states with decreasing temperature, rather it assumes such deviations arise solely from exchange between two $S = \frac{1}{2}$ ions. This assumption was made based on an analysis of the EPR spectrum, which suggested that only the lowest sublevel is populated at low temperature. The $J = \frac{5}{2}$ ground state for a U$^\text{V}$ center is split by the ligand field into three $m_l$ sublevels, two corresponding to $\mu = \pm \frac{1}{2}$ and one corresponding to $\mu = \pm \frac{3}{2}$, where $\mu$ is the crystal quantum number. Considering EPR selection rules, a spectrum is expected for a sublevel with crystal quantum number $\mu = \pm \frac{1}{2}$, while no spectrum is expected for a sublevel with crystal quantum number $\mu = \pm \frac{3}{2}$. The uncoupled dinuclear complex, [(MeC$_5$H$_4$)$_3$U]$_2$(µ-1,3-N$_2$C$_6$H$_4$), gave no EPR spectrum at 4 K, suggesting population of only the lowest-energy sublevel, $\mu = \pm \frac{3}{2}$. Thus, the drop in the magnetic susceptibility of [(MeC$_5$H$_4$)$_3$U]$_2$(µ-1,4-N$_2$C$_6$H$_4$), at least at such very low temperatures, can be attributed to magnetic exchange, rather than the usual effects of the depopulation of excited states. Figure 1.17 shows the resulting calculated and experimental susceptibility data. The differences between the two experimental data sets were attributed to sample impurity and, as such, the calculated data were modeled with varying amounts of paramagnetic impurity. Based on these parameters, the best fit was obtained with an exchange constant of $J = -19$ cm$^{-1}$ and an estimated paramagnetic impurity of 1 mol %. A newer model employs a Hamiltonian that allows for differentiation of the true spins from the effective (due to spin-orbit coupling) spins. This model gives a coupling parameter of $J = -90$ cm$^{-1}$.

1.5.2 Other Multiuranium Systems

Although our focus is on actinide-containing molecules for which the occurrence of magnetic coupling has been directly probed, there are a number of intriguing multiuranium systems wherein magnetic exchange is likely, but has not been rigorously investigated.
example, attempts to produce clusters that might feature uranium-uranium bonds led to a number of simple diuranium alkoxides, including \([U_2(O_2CMe_3)]^{0/1}\), and the chloro-bridged species \([(C_6Me_6)U_2Cl_7]^-\). Based on the assumption that nitrogenous ligands promote bridging in actinides, a number of di-, tri-, and tetranuclear uranium amide species were synthesized, including the dinuclear complex \([U(\eta^4-C_8H_8)]_2[\mu-\eta^4:4-HN(CH_2)_3N(CH_2)_2N(CH_2)_3NH]\), which contains the shortest \(U\cdots U\) separation yet observed in a molecule. Diuranium systems featuring an arene bridge, such as \([(Mes(tBu)N)U]_2(\mu-\eta^6:6-C_7H_8)\) and \([(Cp^*U)]_2(\mu-\eta^6:6-C_6H_6)\), and the pyrazolate-bridged dimer \([U(Me_2Pz)_4]_2\) \((Me_2Pz^- = 3,5	ext{-dimethylpyrazolate})\) also present the strong possibility of magnetic exchange coupling.

Figure 1.18. Structure of \(Cp^* U[(NC(CH_2C_6H_5)tpy)YbCp^*]_2\). Orange, purple, blue, and gray spheres represent U, Yb, N, and C atoms, respectively; H atoms are omitted for clarity. The \(Cp^*\) ligands and benzyl groups are drawn transparently for better visualization of the core structure.

While the foregoing examples constitute only a fraction of the molecular uranium clusters that might exhibit magnetic exchange coupling, they do serve to give an idea of how much synthetic work has already been accomplished in the area. In addition, symmetric dinuclear complexes such as these would serve well in testing general electronic structure models attempting to account for the influence of exchange coupling on the magnetic behavior of actinide ions. Given the current lack of reliable models, a significant step toward probing the presence of exchange coupling in such species would be the development of synthetic methods for preparing mixed-actinide analogues, wherein one of the two actinide centers is rendered diamagnetic. Here, the replacement of one of the \(U^{IV}\) centers with a \(Th^{IV}\) center, or one of the \(U^{III}\) centers with an \(Ac^{III}\) center, would enable a subtraction approach of the type elaborated below to be applied in providing a qualitative assessment of the exchange coupling.
Another type of uranium-containing molecule that offers promise in the area of molecular magnetism is the high-nuclearity uranium oxo cluster. While most oxo-bridged uranium complexes are di- or trinuclear species, it was recently shown that hydrolysis of $\text{U}_{13}(\text{THF})_4$ in the presence of water and other ligands can result in higher-nuclearity clusters. The largest of these is the discrete dodecanuclear species $\text{U}_{12}(\mu_3-\text{O})_{12}(\mu_3-\text{OH})_8\text{I}_{2}(\mu_2-\text{O}_3\text{S}\text{CF}_3)_{16}(\text{CH}_3\text{CN})_8$, which contains a double-decker square antiprism $\text{U}_{12}\text{O}_{12}(\text{OH})_8$ core. This type of cluster, while well beyond the scope of current techniques for analyzing magnetic exchange coupling, may offer prospects for observation of single-molecule magnet behavior in uranium systems. Indeed, such clusters could potentially combine the desirable properties of large spin and single-ion anisotropy with the high coupling strength of the oxo bridge.

1.5.3 A Uranium-Lanthanide System

Recently, evidence of exchange coupling was reported for the bent trinuclear 4f-5f cluster $\text{Cp}^+\text{U}[(\text{NC(CH}_2\text{C}_6\text{H}_5)\text{tpy})\text{YbCp}^+\text{]}_2$ (UYb$_2$; tpy = terpyridyl). The structure of this species features a central $[\text{Cp}^+\text{U}^{IV}]^{2+}$ unit connected through $\text{NC(CH}_2\text{C}_6\text{H}_5)\text{tpy}$ bridges to two $[\text{Cp}^+\text{Yb}^{x+}]^{x+}$ ($x = 0$ or 1) moieties, as shown in Figure 1.18. The cyclic voltammetry and electronic absorption spectra of the UYb$_2$ cluster suggest the presence of both $\text{Cp}^+\text{Yb}^{II}\text{tpy}$ and $\text{Cp}^+\text{Yb}^{III}\text{tpy}$ species at room temperature. The variable-temperature magnetic susceptibility data obtained for the cluster are plotted in Figure 1.19. Here, $\chi_M T$ follows a gradual downward trend from 350 K to ca. 25 K, followed by a precipitous drop at lower temperatures, which can be understood largely in terms of the orbital angular momentum quenching discussed above for 5f$^1$ systems. However, the gradual decline in $\chi_M T$ from its room temperature value is characteristic of multielectron f-element-containing complexes, and is generally attributed to thermal depopulation of low-lying excited states. At extremely low temperature, this effect leads to a quenching of the total angular momentum, thus giving a singlet magnetic ground state for a 5f$^2$ configuration. However, the behavior observed here is further complicated by the presence of both diamagnetic Yb$^{II}$ and paramagnetic Yb$^{III}$ ions, in addition to an unpaired electron residing on the terpyridine fragment.
In an attempt to deconvolute the magnetic data and extract information regarding potential exchange interactions between the U IV and Yb III centers, a stepwise series of subtractions was performed on the UYb2 data. First, $\chi_M^T$ data collected for the precursor complex Cp*2U(NC(CH2C6H5)tpy)2 were subtracted from the UYb2 data to remove any orbital contribution from the U IV ion to the overall magnetism. Then, to eliminate the magnetic contribution from Yb III, $\chi_M^T$ data collected for Cp*2Th[(NC(CH2C6H5)tpy)YbCp*2]2 (ThYb2) were subtracted. The result of these subtractions, shown as $\Delta\chi_M^T$ in the inset of Figure 1.19, is a dataset that follows a monotonic increase with decreasing temperature from 350 K to ca. 15 K, then drops precipitously at lower temperatures. The rise in $\Delta\chi_M^T$ is interpreted as evidence of exchange coupling within the cluster, although the specific nature of the coupling is unclear, as the U IV and Yb III ions and the terpyridine radical represent three distinct paramagnetic centers. The curvature of the data above 60 K is attributed to electronic differences between the UYb2 and ThYb2 clusters, as evidenced in cyclic voltammetry, where the redox peaks for the two clusters are shifted relative to one another. Furthermore, the authors note that the negative values for $\Delta\chi_M^T$ represent an overcorrection during the subtraction process. Thus, while qualitative interpretation of $\Delta\chi_M^T$ vs. $T$ suggests the presence of magnetic coupling, the complexity of this system may prohibit a quantitative analysis.

The magnetic properties of an analogous trinuclear species, Cp*6U3(NC(CH2C6H5)tpy)2, in which U III replaces both of the Yb centers, exhibits a similar trend where $\chi_M^T$ decreases with decreasing temperature. However, the complications encountered in the data analysis of the UYb2 species, along with the lack of diamagnetic analogues to the U IV U III 2 cluster, have thus far made it impossible to deconvolute the many factors contributing to the magnetic susceptibility and isolate evidence of magnetic exchange coupling.

Figure 1.19. Variable-temperature magnetic susceptibility data for Cp*2U[(NC(CH2C6H5)tpy)YbCp*2]2. Inset: Variable-temperature magnetic susceptibility data obtained upon subtracting data for Cp*2U(NC(CH2C6H5)tpy)2 and Cp*2Th[(NC(CH2C6H5)tpy)YbCp*2]2 from the UYb2 data. Taken from Ref 45.
1.5.4 Uranium-Transition Metal Systems

To date, the most comprehensively studied class of actinide-containing molecules exhibiting magnetic exchange interactions is a series of trinuclear uranium-transition metal assemblies synthesized by Ephritikhine and coworkers. These clusters have the form \( \text{UL}^2_M^2 \text{(py)}_n \) (\( M = \text{Cu}, \text{Zn}; \text{py} = \text{pyridine} \)), where \( L^i \) is one of a series of nine Schiff-base bridging ligands, each with a modified diimino hydrocarbon backbone (see Figure 1.20).\(^{46}\) The structure of each cluster consists of a central \( \text{UIV} \) ion coordinated linearly to two \( \text{MII} \) ions through orthogonal \( (L^i)^4^- \) bridges, as represented in Figure 1.21. The \( \text{UIV} \) center resides in a dodecahedral coordination environment, encapsulated by eight oxygen donor atoms. Each \( \text{MII} \) center is coordinated to two nitrogen atoms and two oxygen atoms of the Schiff base in a distorted square planar geometry and is bound by zero, one, or two pyridine molecules, depending on the bridging ligand. Importantly, the coordination environment around the \( \text{UIV} \) center remains invariant with changes in the bridging ligand and number of transition metal-coordinated

![Figure 1.20](image)

**Figure 1.20.** Schematic representation of the ligand precursors \( \text{H}_4L^i \). Note the two-carbon backbone for \( i = 1-5 \), three-carbon backbone for \( i = 6-8 \), and four-carbon backbone for \( i = 9 \).
pyridine molecules, suggesting that differences in magnetic behavior across the series are not due to alterations in the ligand field of the uranium ion.

The isolation of isostructural copper and zinc analogues of the $\text{UL}_2\text{M}_2(\text{py})_n$ clusters enabled the use of a subtraction method similar to the one described above, thereby providing a route through which to investigate the magnetic interaction between the U$^{IV}$ and Cu$^{II}$ ions without contamination by single-ion effects of U$^{IV}$. Variable-temperature magnetic susceptibility data for $\text{UL}_2\text{M}_2(\text{py})$ ($\text{M} = \text{Cu}, \text{Zn}$) are shown at the top of Figure 1.22. For the UZn$_2$ cluster, $\chi_M T$ remains essentially constant at 0.8 cm$^3$K/mol as the temperature is lowered from 300 to 100 K, then drops precipitously at lower temperatures, tending toward zero at 2 K. This drop, typical of U$^{IV}$ complexes with a 5f$^2$ valence electron configuration, can be attributed to the depopulation of the excited states and subsequent quenching of total angular momentum, as described above. The $\chi_M T$ data for the UCu$_2$ cluster exhibit a similar trend, holding constant at 1.7 cm$^3$K/mol down to 100 K, before dropping to 0.8 cm$^3$K/mol at 2 K, close to the value of 0.75 cm$^3$K/mol expected for two non-interacting $S=1/2$ Cu$^{II}$ centers with $g=2.00$. Subtraction of the UZn$_2$ data from the UCu$_2$ data (see Figure 1.22, lower), removes any contribution from the U$^{IV}$ ion, leaving only the spin contribution of the two Cu$^{II}$ ions together with any vestiges of magnetic exchange coupling. Indeed, the product of the subtracted data sets displays a monotonic rise with decreasing temperature, reaching a maximum at $\Delta\chi_M T = 0.95$ cm$^3$K/mol. This increase in $\chi_M T$ is attributed to a ferromagnetic exchange interaction between the U$^{IV}$ and Cu$^{II}$ centers. Although the subtracted data led to the qualitative determination of the sign of the exchange constant (J > 0 for ferromagnetic coupling), no attempts to quantify the magnitude of the interaction have been put forth.

Figure 1.21. Structure of $\text{UL}_2\text{Cu}_2(\text{py})$. Orange, green, red, blue and gray spheres represent U, Cu, O, N, and C atoms, respectively; H atoms are omitted for clarity.
While ferromagnetic coupling is observed for UL$^7_2$Cu$_2$(py), the nature of the exchange appears highly dependent on the identity of the bridging Schiff-base and/or number of pyridine molecules coordinated to the copper center, as found upon comparison of the entire series of UM$_2$ clusters. For $i = 6$, 8, and 9, behavior similar to that of UL$^7_2$Cu$_2$(py) was observed, indicative of ferromagnetic coupling. In contrast, for $i = 1$-5, $\Delta \chi_M T$ turns down below 100 K, indicating an antiferromagnetic exchange interaction. The shift from antiferromagnetic to ferromagnetic coupling occurs as the backbone of the Schiff-base increases from two carbon atoms ($i = 1$-5) to three ($i = 6$-8) or four carbon atoms ($i = 9$). This phenomenon is attributed to an increase in the Cu···U distance, which is associated with a lengthening in the diimino chain. It should be noted, however, that the observation of an increased metal separation is based on structural characterization of only four UC$_2$ clusters ($i = 2$, 6, 7, and 9), for which the average Cu···U distances are 3.538, 3.661, 3.641, and 3.647 Å, respectively. In addition, the magnetic behavior may be affected by other exchange pathways, as evidenced by a downturn in $\chi_M T$ below 15 K observed in the analogous ThL$^i_2$Cu$_2$ clusters ($i = 1$, 2) and deviation of the magnetization data for UL$^i_2$Cu$_2$ ($i = 1$-5) at 2 K from the Brillouin function. This weak effect is attributed to a long-range intramolecular Cu···Cu interaction and may play an important role in influencing the overall magnetism. In explaining this behavior, the authors note that similar magnetostructural correlations have been documented in gadolinium-transition metal species, where exchange interactions were found to vary with factors such as Cu···Gd distances and dihedral angles between O-Cu-O and O-Gd-O planes.$^{47}$
Analogous trinuclear clusters of the form UL\textsuperscript{7}M\textsubscript{2}(py)\textsubscript{2} (M = Co, Ni, Zn) were prepared to probe the effect of the transition metal on the overall magnetic properties of the cluster\textsuperscript{42a,b,d}. Application of the subtraction method to these systems gave $\Delta \chi M$ vs. $T$ plots that show behavior suggestive of anti-ferromagnetic coupling between the central U\textsuperscript{IV} ion and the paramagnetic transition metal ions, in contrast to the ferromagnetic coupling exhibited by the UCu\textsubscript{2} cluster. However, as the authors note, spin-orbit effects associated with high-spin Co\textsuperscript{II} centers may complicate the interpretation of the magnetic data for the UCo\textsubscript{2} cluster. Similarly, the downturn

![Figure 1.22. Upper: Variable-temperature magnetic susceptibility data for UL\textsuperscript{7}Cu\textsubscript{2}(py) (filled circles) and UL\textsuperscript{7}Zn\textsubscript{2}(py) (open triangles) clusters. Lower: Variable-temperature magnetic susceptibility data ($\Delta \chi M$ $T$) obtained upon subtracting the UZn\textsubscript{2} data from the UCu\textsubscript{2} data. Adapted from Ref 46b.](image-url)
in the data for the UNi2 cluster could potentially be attributed to zero-field splitting associated with the S= 1 NiIII centers.

In addition to superexchange interactions, there has been a recent report suggesting that magnetic coupling may occur through direct metal-metal orbital overlap in the mixed-valence linear trinuclear cluster [UFeIIFeIII(C5H4NSi(tBu)Me2)4]+. This intriguing molecule, prepared through the one-electron oxidation of UFeII2(C5H4NSi(tBu)Me2)4, exhibits a structure consisting of a central UIV ion coordinated to two 1,1′-bis(amido)ferrocenyl derivatives (see Figure 1.23). Coordination of the UIV to the rigid ferrocenylamido moieties enforces U···Fe distances of 2.9556(5) and 2.9686(5) Å.

Variable-temperature magnetic moment measurements show very different behavior for the UFeII2 and UFeIIFeIII clusters (see Figure 1.24). In the case of the former species, with decreasing temperature, μeff follows the monotonic drop typical for a UIV center with a 5f2 valence electron configuration. In contrast, for the UFeIIFeIII cluster, as the temperature is decreased from 300 K, μeff begins to rise immediately, following a seemingly linear trend until turning over below 20 K. The authors note that the observed behavior is indicative of a magnetic interaction between UIV and FeIII centers. Indeed the result is without precedent, since the spin-orbit coupling and ligand field effects associated with a paramagnetic uranium center usually give rise to a steady decrease in the net magnetic moment as the temperature is lowered, even in systems exhibiting (weak) ferromagnetic exchange interactions. Thus, the steady increase in μeff starting at room temperature could be indicative of an extremely strong ferromagnetic exchange
interaction mediated by direct orbital overlap between the metals. Note, however, that such a linear upward trend in the moment with decreasing temperature could also potentially arise from complications in applying corrections for the diamagnetic contributions of the unusual sample and/or the sample holder. If indeed the upward trend is the result of a strong ferromagnetic interaction, a simple subtraction of the UFéII data from the UFeIIFeIII would not provide an appropriate means of extracting the pure exchange interaction from the overall magnetism, as the added electron imposes a different ligand field on the central UIV ion. Instead, access to a diamagnetic analogue, such as an isostructural species containing CoIII in place of FeIII, could perhaps lend itself to the implementation of the subtraction method and estimation of the coupling strength for this interesting system.

1.5.5 Uranium-Radical Systems.

Thus far, we have discussed exchange interactions between uranium and other paramagnetic metal centers; however, recent years have seen examples of uranium-radical systems showing evidence of magnetic exchange coupling. The first evidence of such an interaction was reported in 2005 in the radical complex Cp*2UIII(tpy). This molecule, which was prepared through a one-electron reduction of [Cp*2UIII(tpy)]I, features a UIII center coordinated by a terpyridyl ligand that houses an additional, delocalized electron. Structural analysis and NMR spectroscopy support the assignments of uranium and ligand oxidation states.

In an attempt to probe potential exchange between the UIII center and the unpaired electron of the reduced ligand, magnetic susceptibility data were collected for both the radical complex and the cationic precursor complex, [Cp*2UIII(tpy)]I. Structural analysis revealed very similar ligand fields for the two species, enabling the use of the subtraction method, wherein the cationic complex data were subtracted from the radical complex data. The resulting $\chi_M T$ data remains essentially constant as the temperature is lowered from 300 K, before decreasing precipitously below 20 K. This interaction is attributed to antiferromagnetic coupling between
the $S=\frac{3}{2}$ UIII center and the unpaired electron residing on the reduced terpyridyl ligand. While no attempt was made to quantify the coupling strength, the low temperature at which the drop in $\chi_M T$ is observed indicates that the interaction is relatively weak. One possible explanation for the exchange being weak is the large separation between the unpaired electron and the UIII center. While the electron is delocalized throughout the terpyridyl ligand, no good resonance form exists wherein the electron resides on a uranium-coordinated nitrogen atom. Alternatively, the drop in $\chi_M T$ may be the result of intermolecular exchange, possibly between radical ligands on neighboring molecules.

A second example of a uranium-radical complex has been found to bind and activate carbon dioxide.\textsuperscript{50} This molecule was prepared by first encapsulating a UIII ion within the pocket of a bulky hexadentate ligand, $(^\text{Ad}\text{ArO})_3\text{tacn}$ $(^\text{Ad}\text{ArOH})_3\text{tacn} = 1,4,7$-tris(3-adamantyl-5-tert-buty1-2-hydroxybenzyl)1,4,7-triazacyclonane), to give the electron-rich, coordinatively-unsaturated complex $(^\text{Ad}\text{ArO})_3\text{tacn}]U$. Exposure of this complex to an atmosphere of CO$_2$ initiates a one-electron transfer from the UIII center to the CO$_2$ ligand to afford $(^\text{Ad}\text{ArO})_3\text{tacn}]\text{UIV}(\text{CO}_2)$, as depicted in Figure 1.25. The structure of the product reveals a remarkable $\eta^1$-OCO coordination to the UIV ion, with U–C–O and O–C–O bond angles of 171.1(2)$^\circ$ and 178.0(3)$^\circ$, respectively. The presence of an unpaired electron residing on the CO$_2$ carbon was inferred largely from the differences in C–O$_\text{terminal}$ versus C–OU bond lengths and shifts in the infrared spectra compared to free CO$_2$, which suggest a bonding scheme comprised of the resonance forms $\text{UIV}=\text{O}=\text{C} \cdot \text{O} \leftrightarrow \text{UIV}–\text{O}≡\text{C}–\text{O}$.

The variable-temperature magnetic susceptibility data for the radical complex were compared to those taken for a related UIV complex, $(^\text{Ad}\text{ArO})_3\text{tacn}]\text{UIV}(\text{N}_2)$. At high temperature, the $\mu_{\text{eff}}$ vs. $T$ plots for the two compounds are virtually superimposable.\textsuperscript{51} As the temperature is decreased, however, the two curves begin to diverge at ca. 120 K. Below this temperature, the data for the azido complex drop sharply, reaching a minimum of ca. 0.7 $\mu_B$ at 5 K. This behavior

![Figure 1.25](image_url)

**Figure 1.25.** Structure of $(^\text{Ad}\text{ArO})_3\text{tacn}]\text{U}(\text{CO}_2)$.\textsuperscript{50} Orange, red, gray, and blue spheres represent U, O, C and N atoms, respectively; H atoms are omitted for clarity.
is consistent with an isolated $5f^2\text{U}^{I\!V}$ center, with the residual magnetic moment most likely arising from temperature-independent paramagnetism. The low-temperature data for the radical complex display a quite different trend. While the moment drops as the temperature is deceased, it does so more gradually than observed for the azido analogue and reaches a minimum of ca. 1.5 $\mu_B$ at 5 K. The difference in magnetic behavior in the two complexes is attributed to the extra electron residing on the CO$_2$ ligand, which accounts for the added magnetic moment at low temperature. However, the observation that the shapes of the two $\mu_{\text{eff}}$ vs. $T$ curves do not deviate above 120 K may suggest the presence of an exchange interaction between the U$^{I\!V}$ and unpaired electron on the CO$_2$. Unfortunately, the subtraction method cannot be applied to this system due to the lack of an analogue of the radical complex that eliminates the radical but preserves the ligand field experienced by uranium. Thus, it seems unlikely that any exchange interactions between the two paramagnetic centers can be wholly extracted from the overall magnetic behavior of the molecule.

Recently, it was found that a related U$^{III}$ species could reduce di-tert-butylbenzophenone to give $\left[\left((\text{t-BuArO})_{3}\text{tacn}\right)\text{U}^{I\!V}\left(\text{OC}^\cdot\text{t-BuPh}_2\right)\right]$. The crystal data and the results of DFT calculations are consistent with an overall structure comprised of four resonance forms, three containing a U$^{I\!V}$ center and an unpaired electron residing on the di-tert-butylbenzophenone fragment, and one featuring a U$^{III}$ center bound to a diamagnetic di-tert-butyl benzophenone. The temperature dependence of the magnetic susceptibility data for this radical complex shows a trend similar to that of the CO$_2$ complex, with the exception of a higher moment at 300 K, which is attributed to a contribution from the U$^{III}$ resonance form. Calculations suggest that coupling between the U$^{I\!V}$ center and the radical ligand is at least physically reasonable, since the computed SOMO of the molecule consists of both metal and ligand character.

Attempts to model the ligand field and extract exchange coupling data by fitting to an appropriate Hamiltonian have been employed for both lanthanide and actinide systems that have a single, well-isolated $m_J$ ground state. However, complications arise when modeling the temperature-dependent magnetic effects due to subtle shifts in the populations of the low-lying electronic structure. Attempting to model many variables can easily lead to overparameterization, so several groups have circumvented these issues by attempting to synthesize a compound isostructural to the molecule of interest, wherein the non-f-element paramagnetic center has been replaced by a diamagnetic one. Then, a subtraction of the two data sets is performed to simulate removal of the orbital and ligand field effects of the f-element ion, thereby exposing any magnetic exchange coupling interactions. Although extremely dependent on small changes in the ligand field, such a model has been applied successfully to numerous lanthanide-containing systems. This subtraction method is also currently the most widely-employed method for interpreting uranium magnetism and will be discussed in detail in Chapters 2 and 3.
1.6 References and Notes


(14) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. *Manuscript in preparation*.


(16) The discussion of the electronic structure of actinides presented here is meant to give an overview of the complexity of such systems and is by no means comprehensive. For a


(18) The resulting sublevel splitting is often referred to as the Stark splitting, and the states themselves are referred to as Stark sublevels. However, Stark’s claim on the nomenclature is dubious at best. His experiments were on the splitting of hydrogen electronic levels in the presence of an external electric field and never dealt with the f-elements or crystal field environment at all. Among others, it was really the experimental work of J. Becquerel and the theoretical work of Bethe and Kramers that established that the splitting of the absorption lines for lanthanides was due to the symmetry of the crystal field. Therefore, it seems somewhat superfluous to rename an effect that is essentially crystal field splitting after Stark.

Reference to the splitting of the $m_J$ degeneracy of the ground state in lanthanides can be traced to J. Becquerel’s work “Introduction to a Theory of Magneto-optical Phenomena in Crystals” (Becquerel J. Z. Phys. 1929, 58, 205), wherein he compares the effect of the electric field created by the environment of the rare earth to a sort of inhomogeneous Stark effect. In doing so he references W. Pauli’s description of the anomalous spectral lines observed in some compounds of mercury (Handbuch der Physik 1922, 23, 248). It seems unlikely that any of the early researchers on the subject would object to Stark’s name being removed from the effect, given Stark’s later rejection of quantum mechanics as “Jewish physics” and intimate involvement with the Nazi party. Therefore, in this manuscript the microstates of spin-orbit coupled $J$ states are simply referred to as $m_J$ states. For further information on Stark, see Leone, M.; Paoletti, A.; Robotti, N. *Phys. perspect.* 2004, 6, 271.


(22) The term “crystal field” will be used throughout this argument to denote the fact that a purely an electrostatic model is being employed. This is opposed to a “ligand field” model where the overlap of wavefunctions leads to bonding and antibonding interactions. While this approximation holds reasonably well for most lanthanide systems, it tends to be less true for the actinides. However, as a qualitative predictor of the basic electronic structure, the model seems to work reasonably well for all f-elements (see, for example, Section 1.4.3).

This discussion neglects the fact that there exist mechanisms whereby the barrier can be shortcut and direct relaxation between opposite $m_J$ components of the ground state can occur. These mechanisms include, in order of their probable (arguably) importance, molecular symmetry, electronic symmetry, long-range dipolar interactions, and nuclear coupling.

Only the Ho(III) ground state of $^5I_8$ state has a higher total angular momentum, however Ho(III) lacks a Kramers ground state, and significant $4f$ anisotropy (see Figure 6).


Note, however, that accomplishing this substitution would involve very serious difficulties stemming from the short half-life of the available Ac isotopes.


(51) Note that $\chi_M T$ provides a sensitive measure of the magnetic moment of a sample, and is related to the perhaps more familiar quantity $\mu_{\text{eff}}$ as follows: $\mu_{\text{eff}} = (8 \chi_M T)^{1/2} \mu_B$.


Chapter 2: Magnetic Exchange Coupling in Chloride-Bridged 5f-3d Heterometallic Complexes Generated via Insertion into a Uranium(IV) Dimethylpyrazolate Dimer

2.1 Introduction

In Chapter 1, the problems associated with measuring exchange coupling in the f-elements were considered. This topic is of vital importance, as recently, a number of single-molecule magnets have been discovered in which lanthanide ions contribute substantially or entirely to the magnetic anisotropy responsible for the relaxation barrier. Unfortunately, high spin ground states that are well-isolated in energy are difficult to achieve in species of this type, since the contracted 4f orbitals of lanthanide ions have little overlap with bridging ligand orbitals, leading to magnetic exchange constants of only a few wavenumbers at best. In contrast, the 5f orbitals of actinide ions can exhibit an increased radial extension relative to the core electron density, potentially enabling stronger magnetic coupling via superexchange. To date, however, there are only a few cases of actinide-containing molecules for which the presence of magnetic exchange coupling has been established. This is due in part to difficulties with interpreting the magnetic susceptibility data, but also to the dearth of approaches for generating multinuclear 5f-3d assemblies. Herein, we present a new strategy for synthesizing halide-bridged 5f-3d clusters, and demonstrate weak ferromagnetic coupling within a linear U\textsuperscript{IV}-Cl-Ni\textsuperscript{II}-Cl-U\textsuperscript{IV} species.

2.2 Experimental

General Considerations. The syntheses and manipulations of the extremely air and moisture sensitive compounds described below were conducted under nitrogen with rigorous exclusion of air and water by Schlenk and glovebox techniques. THF was distilled over sodium and benzophenone. Toluene, hexanes, dichloromethane, and acetonitrile were saturated with N\textsubscript{2}, passed through an activated alumina column, degassed by three freeze-pump-thaw cycles, and were stored under N\textsubscript{2} over 3 Å molecular sieves. Toluene-\textsubscript{d8} and C\textsubscript{6}D\textsubscript{6} (Cambridge Isotope Laboratories) were distilled over NaK alloy and benzophenone and degassed by three freeze-pump-thaw cycles. Methanol was distilled over Mg and I\textsubscript{2} and saturated with N\textsubscript{2}. Cyclam was dried under vacuum (10\textsuperscript{−3} Torr) for 24 h before use. The compound Me\textsubscript{2}PzH (Aldrich) was sublimed under vacuum (10\textsuperscript{−3} Torr) at 70 °C before use. The compound KN(SiMe\textsubscript{3})\textsubscript{2} (Aldrich) was used as received. UCl\textsubscript{4}\textsuperscript{1} was prepared as previously described. The compound (cyclam)NiCl\textsubscript{2} was prepared with a slight modification to the previously described procedure, in that its synthesis was conducted under nitrogen and prepared from anhydrous NiCl\textsubscript{2} in dry MeOH. The compound (cyclam)CuCl\textsubscript{2} was synthesized by modifying the previously published procedure, in that anhydrous CuCl\textsubscript{2} (100 mg, 0.744 mmol) was reacted with cyclam (149 mg, 0.744 mmol) in dry MeOH under a nitrogen atmosphere for 24 h at 50 °C. The mixture was filtered, concentrated, and cooled to −25 °C to afford (cyclam)CuCl\textsubscript{2} as dark purple crystals (46 mg, 18 % crystalline yield). The compound (cyclam)ZnCl\textsubscript{2} was prepared similar to the previous reported procedure by reacting cyclam (490 mg, 2.45 mmol) with ZnCl\textsubscript{2} (344 mg, 2.53 mmol) at 65 °C in dry MeOH (10 mL) for 12 hours under N\textsubscript{2}. The suspension was filtered, the solvent removed under vacuum, and the solid was washed with toluene. The solid was dissolved in hot CH\textsubscript{2}Cl\textsubscript{2} and cooled to −25 °C to afford (cyclam)ZnCl\textsubscript{2} (427 mg, 51% crystalline yield) as white crystals. The unit cell parameters and \textsuperscript{1}H NMR spectra were consistent with those previously...
reported. NMR experiments were conducted with Bruker 300, 400, and 500 MHz spectrometers. IR samples were analyzed as KBr pellets and recorded on a Nicolet Avatar 360 FTIR spectrometer. UV/Vis absorption spectra were measured using quartz cuvettes equipped with Teflon sealable stop cocks and recorded on a Hewlett-Packard 8453 spectrophotometer. Elemental analyses were performed by the analytical laboratories at the University of California, Berkeley.

**Computational Details.** The Amsterdam Density Functional (ADF) suite of programs (version 2006.01) was used for all calculations. The Zeroth Order Regular Approximation (ZORA) to the Dirac Equation was implemented for scalar relativistic corrections and applied to all atomic basis sets. Uranium basis sets were constructed from triple-ζ quality Slater-type functions plus polarization. All other basis sets were constructed from triple-ζ quality Slater-type functions plus two polarization functions. The frozen core approximation was applied to C (1s), N (1s), Cl (2p), and U (5d). The exchange and correlation functional implemented was built from the Local Density Approximation of Vosko, Wilk, and Nusair with the Generalized Gradient Approximation corrections of Perdew, Burke, and Ernzerhof. Orbital visualizations were generated in ADFview.

**X-ray Data Collection, Structure Solution, and Refinement for [U(Me$_2$Pz)$_4$]$_2$·0.5PhMe.** A green crystal of approximate dimensions 0.07 x 0.09 x 0.13 mm was mounted on a Kapton loop and transferred to a Brüker Apex diffractometer and cooled in a dinitrogen stream. The SMART program package was used to determine the unit-cell parameters and for data collection (10 s/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was $P\bar{1}$ and the systematic absences were consistent with the triclinic space groups $P\bar{1}$ and $P\bar{1}$. It was later determined that the centrosymmetric space group $P\bar{1}$ was correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The toluene molecule that co-crystallized was disordered and atoms C(41), C(43), C(44), C(45), and C(46) were included with partial site-occupancy-factors (1/2) to account for an equal distribution over two sites. At convergence, $wR_2 = 0.0992$ and Goof = 1.026 for 547 variables refined against 8552 data. As a comparison for refinement on $F$, $R_1 = 0.0441$ for those 5928 data with $I > 2.0\sigma(I)$.

**KMe$_2$Pz.** Toluene (200 mL) was added to a Schlenk flask that was charged with KN(SiMe$_3$)$_2$ (14.8 g, 0.0743 mol) and Me$_2$PzH (6.82 g, 0.0709 mmol) and the reaction was stirred for 24 h. The white precipitate was separated from the solution by Schlenk filtration and washed three times with toluene. The solid was then washed with hexane, dried under vacuum at 70 °C for 3 h, and KMe$_2$Pz (9.45 g, 99%) was isolated as a white solid. IR: 3099s, 2971s, 2923s, 2861s, 2722w, 1696w, 1502s, 1431s, 1392s, 1308s, 1123w, 1067w, 1029s, 1008w, 964s, 756s, 730s, 662m, 587w cm$^{-1}$. Anal. Calc. for C$_5$H$_7$KN$_2$: C, 44.75; H, 5.22; N, 20.88 %. Found: C, 44.40; H, 5.16; N, 20.77 %.

**[U(Me$_2$Pz)$_4$]$_2$.** A green solution of UCl$_4$ (0.693 g, 1.83 mmol) in THF (5 mL) was added dropwise to a flask that contained a stirring suspension of KMe$_2$Pz (0.981 g, 7.31 mmol) and THF (15 mL) and the color changed to brown and then to green. After the mixture was stirred for 24 h, a gelatinous brown solid was removed from the green solution by filtration through nylon supported filter paper with 0.22 µm pores, and the solvent was removed under reduced pressure (10$^{-3}$ Torr). Toluene was added to the resulting green solid and a brown toluene-
insoluble solid, which was later found to contain K[U(Me2Pz)5]·THF, was separated by filtration and stored in a separate vial (see below). The solvent was removed from the green filtrate under vacuum and the toluene extraction was repeated twice. Dichloromethane was added to the green solid, the solution was filtered through Celite, and, upon removal of the solvent under reduced pressure, 1.01 g (89%) of product was isolated as a green microcrystalline solid. X-ray quality crystals of [U(Me2Pz)4]2 formed over the course of 3 days from concentrated solutions of toluene cooled to −25 °C. 1H NMR (C6D6, 298 K): δ = 2.5 (s, 48H, Me2Pz, $\Delta \nu_{1/2} = 500$ Hz), 10.8 (s, 8H, CH-Me2Pz, $\Delta \nu_{1/2} = 700$ Hz) ppm; (CDCl3, 294 K) δ = 4.6 (s, 48H, Me2Pz, $\Delta \nu_{1/2} = 580$ Hz), 11.6 (s, 8H, CH-Me2Pz, $\Delta \nu_{1/2} = 1000$ Hz) ppm (toluene-d8, 350.2 K) δ = 4.2 (s, 48H, Me2Pz, $\Delta \nu_{1/2} = 78$ Hz), 12.4 (s, 8H, CH-Me2Pz, $\Delta \nu_{1/2} = 86$ Hz); (292.2 K) δ = 5.7 (s, 48H, Me2Pz, $\Delta \nu_{1/2} = 1400$ Hz), 14.2 (s, 8H, CH-Me2Pz, $\Delta \nu_{1/2} = 1100$ Hz); (270.2 K) δ 8.5 (br, s, Me2Pz), 3.6 (bs, s, Me2Pz); (210 K) 14.5 (s, Me2Pz, $\Delta \nu_{1/2} = 3300$ Hz) ppm. IR: 3200w, 3105m, 2976w, 2946s, 2921s, 2871s, 2802m, 2721w, 1569m, 1516s, 1432s, 1365s, 1306s, 1277m, 1153w, 1105m, 1080m, 1054m, 1006s, 957s, 922w, 867m, 781s, 730s, 697w, 650w cm$^{-1}$. Absorption spectrum (CH2Cl2): $\lambda_{\text{max}}$ 330 (sh), 479 (sh), 505 (sh), 557, 620, 676, 823 (sh), 869 (sh), 944 (sh), 1005 (sh) nm. No extinction coefficients are reported since the degree of oligomerization in solution is unclear. Anal. Calcd. for C40H56N16U2·1/2(C7H8): C, 40.07; H, 4.67; N, 17.47. Found: C, 39.87; H, 4.46; N, 17.06.

K[U(Me2Pz)5]·THF. The brown solid that was separated from the toluene extractions in the above synthesis of [U(Me2Pz)4]2 was washed three times with toluene and dissolved in THF. The solution was cooled to −25 °C and after 3 days crystals formed. The mother liquor was decanted, and the crystals were dried under reduced pressure to give 18 mg (1%) of product. Single crystals were grown from saturated solutions of THF at −25 °C. IR: 3202s, 3131s, 3109s, 3039s, 2921s, 2878s, 2792s, 2726m, 2609w, 1672w, 1596m, 1577m, 1517s, 1484s, 1459s, 1418s, 1372m, 1307s, 1265w, 1155w, 1149w, 1100m, 1029s, 1010s, 963m, 854m, 780s, 738m, 730m, 683w, 662m, 553m cm$^{-1}$. Anal. Calcd. for C29H43N10UKO: C, 42.24; H, 5.22; N, 16.99 %. Found: C, 41.88; H, 5.14; N, 16.86 %.

(Me2Pz)4U(THF). THF (1 mL) was added to a flask that contained [U(Me2Pz)4]2 (499 mg, 0.404 mmol) and the solution was filtered. The solution was cooled to −25 °C and after 10 days crystals formed. The solution was decanted from the crystals, they were dried under vacuum, and (Me2Pz)4U(THF) was isolated (180 mg, 32%) in crystalline form. X-ray quality crystals can be grown from a saturated solution of [U(Me2Pz)4]2 in THF at −25 °C. 1H NMR (THF-d8 referenced to an internal standard of C6D6, 298 K): δ = 6.9 (s, 24H, Me3Pz, $\Delta \nu_{1/2} = 320$ Hz), 14.2, (s, 4H, CH-Me2Pz, $\Delta \nu_{1/2} = 1000$ Hz) ppm. No resonances attributable to the coordinated THF ligand were identified. IR: 3201w, 3102m, 2978s, 2951s, 2922s, 2800s, 2723s, 1569m, 1514s, 1456s, 1412s, 1365s, 1307m, 1276m, 1170w, 1153w, 1105m, 1054m, 1024s, 1007s, 958s, 922m, 867s, 808s, 781s, 730s, 673w, 651w cm$^{-1}$. Absorption spectrum (CH2Cl2): $\lambda_{\text{max}}$ 320 (sh), 479 (sh), 505 (sh), 557, 620, 676, 823 (sh), 869 (sh), 944 (sh), 1005 (sh) nm. No extinction coefficients are reported since the degree of oligomerization in solution is unclear. Anal. Calcd. for C29H36N16OU : C, 41.24; H, 5.22; N, 16.99 %. Found: C, 41.88; H, 5.14; N, 16.86 %.

(cyclam)Ni[µCl]U(Me2Pz)4 (NiU2). A green solution of [U(Me2Pz)4]2 (752 mg, 0.608 mmol) in CH2Cl2 (5 mL) was added dropwise to a flask charged with a pink suspension of (cyclam)NiCl2 (200 mg, 0.607 mmol) in CH2Cl2 (5 mL). Everything immediately dissolved and the resulting green solution was stirred for 12 h. The solution was filtered through Celite, concentrated under vacuum to approximately 1 mL, and cooled to −25 °C. After 48 h, the solvent was decanted from the crystals that had formed. The crystals were dried under vacuum,
to give 618 mg (65%) of product. X-ray quality crystals readily form from concentrated solution of CH₂Cl₂ cooled to −25 °C. ¹H NMR (C₆D₆, 294 K): δ = −18.3 (s, 4, C₁₀H₂₄N₄, Δν₁/₂ = 160 Hz) −9.1 (s, 4, C₁₀H₂₄N₄, Δν₁/₂ = 380 Hz), 6.1 (s, 48, Me₂Pz, Δν₁/₂ = 840 Hz) 15.6 (s, 8, HC-Me₂Pz C₃N₂, Δν₁/₂ = 870 Hz), 41 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 870 Hz), 178 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 670 Hz) ppm; (toluene-d₈, 323.1 K): δ = −16.4 (s, 4, C₁₀H₂₄N₄, Δν₁/₂ = 130 Hz) −7.7 (s, 4, C₁₀H₂₄N₄, Δν₁/₂ = 300 Hz), 5.3 (s, 48, Me₂Pz, Δν₁/₂ = 320 Hz), 14.4 (s, 8, CH-Me₂Pz, Δν₁/₂ = 320 Hz), 36.7 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 1020 Hz) 161 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 670 Hz) ppm; (toluene-d₈, 193.1 K): δ = −32.2 (s, 4, C₁₀H₂₄N₄, Δν₁/₂ = 420 Hz), −19.1 (s, 12, Me₂Pz-axial, Δν₁/₂ = 480 Hz), −13.2 (s, 10C₆H₄N₄, Δν₁/₂ = 480 Hz), −16.7 (s, 2, CH-Me₂Pz-axial), 20.0 (s, 36, Me₂Pz-equatorial, Δν₁/₂ = 220 Hz), 33.1 (s, 6, CH-Me₂Pz, Δν₁/₂ = 160 Hz), 54.2 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 1830 Hz) 280 (s, 8, C₁₀H₂₄N₄, Δν₁/₂ = 1300 Hz) ppm. IR: 3265m, 3251s, 3227s, 3137m, 3099m, 3021m, 2921s, 2871s, 2798m, 2721w, 1574m, 1519s, 1461s, 1435s, 1373m, 1365m, 1348m, 1297m, 1254w, 1200s, 1133s, 1077m, 1062m, 1007s, 976s, 887m, 781s, 730s, 651w, 585w cm⁻¹. Absorption spectrum (CH₂Cl₂): λ max (λM) 441 (129), 479 (81), 511 (62), 532 (49), 561 (sh, 33), 625 (51), 660 (sh, 61), 677 (92), 946s, 893w, 878s, 786s (br), 730s, 672w, 651w, 586m, 556m cm⁻¹. Absorption spectrum (CH₂Cl₂ referenced to a C 6D6 internal standard, 298 K): δ = 6.8 (Δν₁/₂ = 670 Hz) 15.6 (Δν₁/₂ = 1000 Hz) ppm. IR: 3369m, 3217s, 3135s, 3099m, 3021m, 2921s, 2871s, 2798m, 2721w, 1574m, 1519s, 1423s, 1365s, 1308m, 1242w, 1154w, 1100s, 1066s, 1029s, 976s, 887m, 781s, 730s, 651w, 585w, 459m, 434s cm⁻¹. Absorption spectrum (CH₂Cl₂): λ max (λM) 481 (82), 513 (86), 556 (73), 611 (57), 677 (67), 865 (29), 924 (30), 1034 nm (48 Lmol⁻¹cm⁻¹). Anal. Calcd. for C₅₀H₈₀Cl₂N₂O₄U₂: C, 38.20; H, 5.14; N, 17.83%. Found: C, 38.04; H, 5.07; N, 17.66%.

**Magnetic Measurements.** Finely dispersed samples were prepared by first adding approximately 100 mg of molten eicosane (Aldrich) to a 7 mm quartz tube. After the eicosane had cooled, crystals of the compounds NiU₂ (95.5 mg), CuU₂ (93.8 mg), and ZnU₂ (105.8 mg),
that had been desolvated under vacuum \(10^{-3}\) Torr to remove the CH$_2$Cl$_2$ solvate molecules, were loaded into the tube and embedded in the eicosane matrix to prevent crystallite torqueing at high magnetic fields. The total amounts of eicosane used were 288.6, 267.8, and 299.9 mg for the samples of NiU$_2$, CuU$_2$, and ZnU$_2$, respectively. Each tube was fitted with a Teflon sealable adapter, attached to a Schenk line, and flame sealed under vacuum.

Figure 2.1. Structure of (Me$_2$Pz)$_4$U(THF). Orange, gray, and blue spheres represent U, C, and N atoms, respectively; H atoms are omitted for clarity.
Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data measurements were performed at temperatures ranging from 5 to 301 K, using applied fields of 0.1, 0.5, and 1 T. Magnetization measurements were performed at temperatures ranging from 1.78 to 10 K, using applied fields from 1 to 7 T at 1 T intervals. Data for NiU$_2$, CuU$_2$, and ZnU$_2$ were corrected for diamagnetic contributions from the sample holder and eicosane, as well as for the core diamagnetism of each sample. These last were estimated using Pascal’s constants to give $\chi_D = -7.75 \times 10^{-4}$, $-7.74 \times 10^{-4}$, and $-7.48 \times 10^{-4}$ emu/mol for NiU$_2$, CuU$_2$, and ZnU$_2$, respectively. A temperature-independent paramagnetism value of 0.000825 cgsu was used for NiU$_2$.

2.3 Results and Discussion

The homoleptic dimer complex [U(Me$_2$Pz)$_4$)$_2$ (Me$_2$Pz$^-$ = 3,5-dimethylpyrazolate) was obtained from a reaction of UCl$_4$ with KMe$_2$Pz in THF. Its formation proceeds under mild conditions, in stark contrast to the more demanding synthetic procedures required for generating homoleptic lanthanide pyrazolates. Depending on reaction conditions, two additional products were isolated and analyzed by X-ray crystallographic analysis: a THF adduct, (Me$_2$Pz)$_4$U(THF) (Figure 2.1), and a salt of the pentapyrazolate uranium(IV) complex, K[U(Me$_2$Pz)$_5$]·THF (Figure 2.2). Despite the propensity of uranium(IV) for binding THF, the dimer can be isolated in high yield by repeated extractions into toluene. The pentapyrazolate byproduct is insoluble in toluene, and its yield was minimized by adjusting the reaction stoichiometry to precisely four equivalents of unsolvated KMe$_2$Pz per equivalent of UCl$_4$. 

Figure 2.2. Structure of the pentapyrazolate uranium(IV) 1D chain, K[U(Me$_2$Pz)$_5$]·THF. Orange, purple, red, gray, and blue spheres represent U, K, O, C, and N atoms, respectively; H atoms are omitted for clarity.
Green needle-shaped crystals of \([\text{U(Me_2Pz)_4}]_2\cdot 0.5\text{PhMe}\) formed upon cooling a saturated toluene solution of the dimer, and X-ray analysis revealed the structure depicted in Figure 2.3. Here, considering each pyrazolate ligand as a single entity, the U^{IV} centers adopt a trigonal bipyramidal coordination geometry. Two of the ligands, one equatorial and one axial, form asymmetric bridges, with the latter exhibiting the more elongated U-N bonds of 2.616(7) and 2.719(7) Å. To our knowledge, this is the first example of a homoleptic pyrazolate complex of an actinide element. Related dimeric structures in which each metal center bears just two terminal pyrazolate ligands have been observed, for example, in \([\text{Ln(Bu_2Pz)_3}]_2\) (Ln = La, Nd, Yb, Lu). In contrast to the tetravalent uranium ions, the trivalent lanthanide ions exhibit a coordination geometry intermediate between square planar and tetrahedral, with cases of both symmetric and asymmetric pyrazolate bridging modes arising.

Bases are capable of cleaving the uranium(IV) dimer via displacement of the axial bridging pyrazolate ligands. For example, reaction with THF yields the pseudo trigonal bipyramidal complex \((\text{Me_2Pz})_4\text{U(THF)}\), wherein THF occupies an axial coordination site. More interestingly, the dimer can be cleaved via insertion of a terminal chloride ligand of a transition metal complex. In particular, reactions with \((\text{cyclam})\text{MCl}_2\) (M = Ni, Cu, Zn; cyclam = 1,4,8,11-tetraazacyclotetradecane) in dichloromethane generate the trinuclear species \((\text{cyclam})\text{M}[\mu-\text{Cl})\text{U(Me_2Pz)_4}]_2\). Note that this is consistent with the established halophilicity of uranium(IV), and that, fortunately, in these cases, complete chloride abstraction does not occur. While there are examples of molecular compounds with halide ligands bridging between uranium(IV) and...

**Figure 2.3.** The uranium(IV) 3,5-dimethylpyrazolate dimer. Orange, grey, and blue spheres represent U, C, and N atoms, respectively; H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) for \([\text{U(Me_2Pz)_4}]_2\): mean U-N\text{terminal} 2.37(3), U-N\text{bridging} 2.489(7)-2.719(7), U···U 3.9485(5), mean U-N-U 99.1(7), U-N\text{bridging-C} 116.5(6)-119.8(5), 140.9(6)-144.2(6).
alkali metal cations,\textsuperscript{11} to our knowledge these are the first examples of halide-bridged species involving uranium(IV) and transition metal ions.

Cooling saturated solutions of the products afforded a set of isostructural crystals, featuring the intended linear, chloride-bridged clusters (see Figure 2.4). Here, a $\text{U(Me}_2\text{Pz)}_4$ unit is appended to each of the trans chloride ligands of a central (cyclam)$\text{MCl}_2$ complex. In comparing the three structures, the most obvious difference lies in the variation of the $\text{M}^{\text{II}}$-Cl distances, with a Jahn-Teller distortion leading to a significantly longer $\text{Cu}^{\text{II}}$-Cl separation. Importantly, the U-Cl-M angle and U$^{\text{IV}}$ coordination environment show little variation as M changes. Thus, the species containing the diamagnetic Zn$^{\text{II}}$ ion can be used as a reasonable model in accounting for the U$^{\text{IV}}$ contributions to the magnetism of the other clusters. Note that such an approach is necessitated by the lack of a suitable theoretical construct for predicting the temperature dependence of the magnetic moments of the constituent actinide ions. This method has been employed previously in probing exchange coupling in bridged uranium(IV)-transition metal complexes,\textsuperscript{5b-f} and is commonly applied in evaluating compounds containing lanthanide ions with unquenched orbital angular momentum.\textsuperscript{3c}

Variable-temperature magnetic susceptibility data were measured for all three trinuclear complexes (see Figure 2.5). The data for the ZnU$_2$ cluster exhibit a steady drop in $\chi_M T$ as the temperature is lowered, decreasing from 2.16 emu·K/mol at 298 K to 0.10 emu·K/mol at 5 K.\textsuperscript{12} This behavior is typical of 5f$^2$ U$^{\text{IV}}$ complexes, and the reduction in moment at lower temperatures is consistent with a poorly-isolated singlet ground state arising from crystal field effects.\textsuperscript{13} For the CuU$_2$ cluster, the data show a nearly identical temperature dependence, but with increased $\chi_M T$ values. By subtracting the ZnU$_2$ data from the CuU$_2$ data, the individual U$^{\text{IV}}$ contributions are removed, leaving the magnetism of the central $S = 1/2$ Cu$^{\text{II}}$ ion, together with any vestiges of magnetic exchange coupling. The subtracted data, shown in red, reveal a moment that is essentially invariant with temperature, affording a mean value of $\chi_M T = 0.36(2)$ emu·K/mol ($\mu_{\text{eff}} = 1.70(4) \mu_\text{B}$). The results are consistent with a Cu$^{\text{II}}$ ion in the absence of any magnetic exchange coupling, albeit with a moment that is slightly below the usual value for a
pseudooctahedral complex. For comparison, (cyclam)CuCl$_2$ was observed to display a mean value of $\chi_M T = 0.43(1)$ emu·K/mol ($\mu_{\text{eff}} = 1.84(1)$ $\mu_B$).$^{14}$ The slight difference may be associated with the change in ligand field arising upon attachment of a U$^{IV}$ center to each chloride ligand, and perhaps with the presence of a small amount of diamagnetic impurity. The sole unpaired electron of the Cu$^{II}$ center of the CuU$_2$ cluster resides in the $d_{x^2-y^2}$ orbital, which has $\delta$ symmetry with respect to the Cu-Cl bonds. Thus, the lack of exchange coupling can be explained as arising from the orthogonality of the Cu$^{II}$ spin orbital with $\sigma$- and $\pi$-type orbitals of the chloride bridges. The complete invariance of the subtracted data affirms that the ZnU$_2$ cluster serves well in partitioning out the magnetism of the U$^{IV}$ centers.

Figure 2.5. Variable temperature magnetic data for the linear clusters (cyclam)M[(μ-Cl)U(Me$_2$Pz)$_4$]$_2$ (M = Ni (green), Cu (blue), Zn (black)).$^{12}$ The data sets shown in red were obtained upon subtracting the Zn data from the Cu data (upper) and Ni data (lower). The solid line represents a fit to the latter data, as discussed in the text.
As shown at the bottom of Figure 2.5, the $\chi_M T$ data for the NiU$_2$ cluster display a quite different temperature dependence. Subtracting the ZnU$_2$ data affords a $\chi_M T$ value of 1.19 emu·K/mol at 298 K, consistent with the presence of an $S = 1$ Ni$^{II}$ ion having $g = 2.18$. Below 100 K, the subtracted data increases, achieving a maximum of 1.26 emu·K/mol at 30 K. This rise in moment is not expected for an isolated Ni$^{II}$ center, and indicates the presence of ferromagnetic exchange interactions. In order to assess the strength of the exchange coupling, a simple spin-only model was adopted. A temperature-invariant contribution of $\chi_M T = 1.00$ emu·K/mol for each U$^{IV}$ center was added back into the subtracted data (see Figure 2.6). Utilizing MAGFIT 3.115 and a spin Hamiltonian of the form $\hat{H} = -2J \hat{S}_{Ni} (\hat{S}_{U(1)} + \hat{S}_{U(2)}) + g\mu_B S \cdot B$, the data above 40 K were then fit to give the parameters $J = 2.3$ cm$^{-1}$, $g = 1.86$, and TIP = $8.25 \times 10^{-4}$ emu/mol. To our knowledge, this represents the first estimate of a 5f-3d coupling constant within a molecular complex. Note, however, that the treatment provides only a lower bound for $J$. The actual $J$ value is likely substantially higher, since we have not accounted for the gradual loss of spin on the U$^{IV}$ centers with decreasing temperature.

The drop in $\chi_M T$ for the subtracted data below 30 K stems in part from this loss of U$^{IV}$ spin, but probably also from a zero-field splitting contribution to the ground state. Indeed, variable-field magnetization data collected at low temperatures reveal large separations between iso-field lines (see Figure 2.7), as typically associated with a significant axial zero-field splitting. Despite this large anisotropy, ac magnetic susceptibility measurements carried out at temperatures down to 1.8 K with switching frequencies of up to 1500 Hz showed no out-of-phase signal attributable to single-molecule magnet behavior.
Density functional theory calculations were performed on a \([(\text{Me}_2\text{Pz})_4\text{UCl})^-\] fragment of the NiU$_2$ cluster to determine the symmetry of 5f orbitals involved in magnetic exchange. Assuming the z axis is oriented along the U-Cl bond, the spin-containing orbitals are 5f$_{\text{xyz}}$ and 5f$_{\text{z}(x^2-y^2)}$ (see Figure 2.8). Importantly, both of these orbitals exhibit δ symmetry with respect to the U-Cl bond, such that they are rigorously orthogonal to the Ni$^{\text{II}}$ 3d$_{z^2}$ spin feeding through σ-type Cl$^-$ orbitals. Thus, the observed ferromagnetic coupling is consistent with a simple superexchange mechanism.

The foregoing results disclose a potentially generalizable means of assembling 5f-3d clusters, and demonstrate weak ferromagnetic coupling between U$^{\text{IV}}$ and Ni$^{\text{II}}$ through a chloride bridge. Future investigations will focus on utilizing this synthetic approach to achieve higher-nuclearity clusters, as well as to enhance exchange coupling via introduction of either bromide or iodide bridges, or lower-valent uranium centers. We note that each of these directions presents significant synthetic difficulties,\textsuperscript{16} and that the utilization of actinide elements in generating high-anisotropy single-molecule magnets therefore remains a daunting challenge. The results of one of these investigations, the formation of lower-valent uranium complexes, will be returned to in chapter 4.

![Figure 2.7](image.png)

**Figure 2.7.** A plot of reduced magnetization, $M/N\mu_B$ (where $N$ is Avogadro’s number and $\mu_B$ is the Bohr magneton) versus $H/T$ for (cyclam)Ni[(μ-Cl)U(Me$_2$Pz)$_4$]$_2$. Data were measured from 1.8 to 10 K and at the seven field strengths specified.
2.4 Acknowledgement

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2.5 References and Notes


![Figure 2.8. Frontier energy level diagram and depictions of the spin-containing molecular orbitals, as calculated for [(Me₂Pz₄)₄UCl]⁺ using density functional theory. The Me₂Pz⁻ ligands are shown as skeletal representations, and the U-Cl axis is oriented vertically.](image-url)


(12) Note that $\chi_M T$ provides a sensitive measure of the magnetic moment of a sample, and is related to the perhaps more familiar quantity $\mu_{\text{eff}}$ as follows: $\mu_{\text{eff}} = (8 \chi_M T)^{1/2} \mu_B$.

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(16) The generation of related species containing lower-valent uranium centers can be seen to present particular difficulties, given the strong reducing power of $U^{III}$. Evans, W. J.; Kozimor, S. A. Coord. Chem. Rev. 2006, 250, 911.
Chapter 3: Ferromagnetic Exchange Coupling in the Linear, Chloride-Bridged Cluster (cyclam)\(\text{Co}^{II}[(\mu{-}\text{Cl})\text{U}^{IV}(\text{Me}_2\text{Pz})_4]\)2

3.1 Introduction

In Chapter 2, a methodology for synthesizing discrete isostructural complexes of the form (cyclam)\(M[(\mu{-}\text{Cl})\text{U}(\text{Me}_2\text{Pz})_4]\)2 (\(M = \text{Ni}, \text{Cu}, \text{Zn} \); cyclam = 1,4,8,11-tetraazacyclotetradecane, \(\text{Me}_2\text{Pz}^- = 3,5\)-dimethylpyrazolate) was presented. Magnetic analysis of such systems is valuable to the advancement of single-molecule magnet research, since the f-elements should be well-suited for maximizing axial anisotropy due to increased coupling between spin and orbital angular momenta.\(^1\) Actinides in particular offer an intriguing alternative to transition metals for single-molecule magnet synthesis, in that the single-ion anisotropy should be greatly increased, while magnetic exchange coupling remains viable due to the radial extension of the 5f orbitals.\(^2\) Despite these advantages, quantitative studies of magnetic coupling in actinide-containing systems remain relatively rare\(^3\) due to the innate complications of the large spin-orbit coupling present in actinide elements. Herein, we present the synthesis of a new chloride-bridged 5f-3d trinuclear cluster, (cyclam)\(\text{Co}[(\mu{-}\text{Cl})\text{U}(\text{Me}_2\text{Pz})_4]\)2, and use the empirical methodology for isolating the effects of exchange coupling employed in Chapter 2 to demonstrate that it has the strongest ferromagnetic coupling of the series.

3.2 Experimental

General considerations. The syntheses and manipulations of the extremely air and moisture sensitive compounds described below were conducted under nitrogen with rigorous exclusion of air and water by Schlenk and glovebox techniques. Dichloromethane was saturated with \(\text{N}_2\), passed through an activated alumina column, degassed by three freeze-pump-thaw cycles, and stored under \(\text{N}_2\) over 3-Å molecular sieves. Benzene-\(d_6\) (Cambridge Isotope Laboratories) was distilled over sodium-potassium alloy with benzophenone and degassed by three freeze-pump-thaw cycles. Methanol was distilled over magnesium and iodine and saturated with \(\text{N}_2\). The compounds [\(\text{U}(\text{Me}_2\text{Pz})_4]\)_2 and (cyclam)\(M[(\mu{-}\text{Cl})\text{U}(\text{Me}_2\text{Pz})_4]\)2 (\(M = \text{Zn}, \text{Ni}\)) were synthesized as previously described.\(^3\)\(^g\) NMR spectroscopy experiments were conducted using a Bruker 400 MHz spectrometer. UV-vis absorption spectra were measured in 1-cm path length quartz cuvettes equipped with Teflon sealable stopcocks and recorded on a Cary 5000 spectrophotometer. Elemental analyses were performed by the analytical laboratories at the University of California, Berkeley.

Magnetic measurements. Powder microcrystalline magnetic samples were prepared in a frozen eicosane matrix and sealed in quartz tubes under vacuum. Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data measurements were performed at temperatures ranging from 5 to 300 K, using applied fields of 0.1, 0.5, and 1 T. Magnetization measurements were performed at temperatures ranging from 1.8 to 10 K under an applied magnetic field varying from 1 to 7 T at 1 T intervals.

All magnetic data were corrected for the diamagnetic contributions from the quartz sample holder and eicosane, as well as for the core diamagnetism of each sample. Core diamagnetism was estimated using Pascal’s constants to give \(\chi_D = -2.13 \times 10^{-4}, \ -7.75 \times 10^{-4}\), and \(-7.78 \times 10^{-4}\) emu/mol for (cyclam)\(\text{CoCl}_2\), (cyclam)\(\text{Co}[(\mu{-}\text{Cl})\text{U}(\text{Me}_2\text{Pz})_4]\)_2, and (cyclam)\(\text{Zn}[(\mu{-}\text{Cl})\text{U}(\text{Me}_2\text{Pz})_4]\)_2, respectively.
X-ray crystallography. Crystallographic data for (cyclam)Co[µ-Cl]U(Me₂Pz)₄]₂·4CH₂Cl₂ are presented in Table 1. A crystal was mounted on a Kapton loop and transferred to a Bruker APEX diffractometer and cooled in a nitrogen stream. The SMART program package was used to determine the unit cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). Data integration was performed by SAINT and the absorption correction provided by SADABS. Subsequent calculations were carried out using the SHELXTL program. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

(cyclam)CoCl₂. A solution of CoCl₂ (50 mg, 0.39 mmol) in 3 mL of methanol was added dropwise to a solution of cyclam (77 mg, 0.39 mmol) in 3 mL of methanol to form a pink solution. After stirring for 3 h, the solution was cooled to −25 °C for 24 h. The resulting pink needle-like crystals were collected by filtration and washed with methanol (3 × 5 mL). The crystals were then dried under reduced pressure at 50 °C for 3 h to give 81 mg (64%) product.

Anal. Calcd. for C₁₀H₂₄Cl₂CoN₄: C, 36.38; H, 7.33; N, 16.97 %. Found: C, 36.34; H, 7.51; N, 16.54 %.

(cyclam)Co[µ-Cl]U(Me₂Pz)₄]₂. A solution of [U(Me₂Pz)₄]₂ (200 mg, 0.16 mmol) in dichloromethane (8 mL) was added dropwise to a solution of (cyclam)CoCl₂ (54 mg, 0.16 mmol) in dichloromethane (8 mL) to form a green solution. After stirring for 12 h, the solution was filtered through Celite, concentrated to approximately 5 mL under reduced pressure, and cooled to −25 °C for 24 h. The resulting green block-shaped crystals were isolated by decanting the green supernatant solution. The crystals were dried under reduced pressure to give 110 mg (43%) of product. H NMR (CH₂Cl₂ referenced to a C₆D₆ internal standard, 292 K): δ−36 (Δν₁/₂ = 3200 Hz), −15 (Δν₁/₂ = 2000 Hz) 6 (Δν₁/₂ = 280 Hz), 15 (Δν₁/₂ = 800 Hz) ppm. Accurate integrations and peak assignments were not possible due to the paramagnetic nature of the complex. Absorption spectrum (CH₂Cl₂): λmax (εₘ) 234 (5965), 328 (sh, 4030), 479 (66), 506 (45), 562 (19), 626 (32) 678 (67), 870 (17), 924 (18) nm. Anal. Calcd. for C₅₀H₈₀Cl₂CoN₂₀U₂: C, 38.31; H, 5.16; N, 17.88 %. Found: C, 38.43; H, 5.34; N, 17.92 %.
3.3 Results and Discussion

Cleavage of the [U(Me$_2$Pz)$_4$)$_2$ dimer by (cyclam)CoCl$_2$ affords the trinuclear cluster (cyclam)Co[(µ-Cl)U(Me$_2$Pz)$_4$]$_2$ in moderate yield. The structure (see Figure 3.1) is centrosymmetric with an inversion center located on the central cobalt atom; four CH$_2$Cl$_2$ molecules also occupy the unit cell. The metric parameters of the cluster are listed in Table 2 together with those of the previously synthesized analogues (cyclam)M[(µ-Cl)U(Me$_2$Pz)$_4$]$_2$ (M = Ni, Cu, Zn) for comparison. Of particular note, the structure of the CoU$_2$ cluster is extremely similar to that of the ZnU$_2$ cluster, such that the latter can be used as a reasonable model in accounting for the U$^{IV}$ contributions to the magnetism of the former. The similarity between the 2.680(2) and 2.680(2) Å M–Cl (M = Co and Zn) distances in CoU$_2$ and ZnU$_2$, respectively, is somewhat unexpected, since the observed Co–Cl distance is significantly longer than analogous bond lengths typically observed (2.282-2.522 Å) in species featuring Co$^{II}$ centers bridged to another transition metal through chloride. We note in our previous study of NiU$_2$ and CuU$_2$, that the Ni–Cl distance of 2.564(2) Å engenders ferromagnetic coupling between Ni$^{III}$ and U$^{IV}$, but that the long Cu–Cl distance of 2.774(2) Å gives rise to a complex that shows no magnetic coupling. In CoU$_2$, the Co–Cl distance is intermediary while the 1.973(14) Å average Co–N distance is similar to the analogous distances in the NiU$_2$ and CuU$_2$ complexes, cf. 2.061(3) and 2.020(4) Å, respectively. This suggests that magnetically, the system might be best described as containing a low-spin ($S=1/2$) Co$^{II}$ complex with the longer Co–Cl bond distances arising from a 1$^{st}$ order Jahn-Teller distortion. This unpaired electron resides in $d_{z^2}$ and is therefore oriented directly along the superexchange pathway. This may provide sufficient orbital overlap to open the possibility of magnetic coupling despite the unusually long Co–Cl bond distance. In contrast, for CuU$_2$, the Jahn-Teller distortion results in an elongated Cu–Cl bond where the unpaired electron occupies $d_{x^2-y^2}$, orthogonal to the exchange pathway.
As an initial probe of the spin of Co\textsuperscript{II} center in the cluster, we collected magnetic susceptibility data of the precursor complex (cyclam)CoCl\textsubscript{2}. Figure 3.2 shows the resulting $\chi_M T$ product of 0.41 emu·K/mol, which is essentially invariant with temperature, indicative of an $S=\frac{1}{2}$ compound. The lack of variance in $\chi_M T$ with temperature obviates the likelihood that spin-orbit coupling in high-spin Co\textsuperscript{II} results in the observed $S=\frac{1}{2}$ behavior\textsuperscript{11}, since this normally only occurs through a gradual depopulation of the excited spin-orbit coupled state at low temperature ($<40$ K). The simple $S=\frac{1}{2}$ nature of the Co\textsuperscript{II} will greatly simplify the modeling of the magnetic data for the CoU\textsubscript{2} cluster by eliminating the need to account for Co\textsuperscript{II} spin-orbit coupling.

The problems associated with interpreting f-element magnetic behavior arise from a confluence of factors. The predominant issue is the breakdown of the spin-only approximation arising from coupling of the orbital angular momentum to the spin angular momentum within the quasi-degenerate $f$-orbitals. In addition, however, actinide elements tend to display greater covalency in their bonding than lanthanide elements, such that spin loss resulting from the presence of ligand field effects cannot be ignored. The ligand field, albeit weak, removes the degeneracy of the $f$-orbitals and gives rise to low lying excited states that factor in a complicated way into the temperature dependence of the magnetic susceptibility. The magnetic susceptibility

\begin{table}[h]
\centering
\begin{tabular}{l|l}
\hline
\textbf{Empirical formula} & U\textsubscript{2}CoCl\textsubscript{10}N\textsubscript{20}C\textsubscript{64}H\textsubscript{88} \\
\hline
\textbf{Formula weight} & 1906.93 \\
\textbf{Temperature} & 166(2) K \\
\textbf{Wavelength} & 0.71073 Å \\
\textbf{Crystal system} & triclinic \\
\textbf{Space group} & $\bar{P}$ \\
\textbf{Unit cell dimensions} & \\
\textbf{$a$ (Å)} & 11.440(3) \\
\textbf{$b$ (Å)} & 12.178(4) \\
\textbf{$c$ (Å)} & 14.903(4) \\
\textbf{$\alpha$ (°)} & 72.408(5) \\
\textbf{$\beta$ (°)} & 77.100(5) \\
\textbf{$\gamma$ (°)} & 73.871(4) \\
\textbf{Volume (Å\textsuperscript{3})} & 1879.1(10) \\
\textbf{$Z$} & 1 \\
\textbf{$D_{calc}$ (Mg/m\textsuperscript{3})} & 1.685 \\
\textbf{Absorption coefficient (mm$^{-1}$)} & 4.920 \\
\textbf{Crystal size (mm)} & 0.13 \times 0.12 \times 0.03 \\
\textbf{$\theta$ Range for data collection (°)} & 1.45 to 23.32 \\
\textbf{Data / restraints / parameters} & 5386 / 0 / 394 \\
\textbf{Final Rindices [/ > 2σ(I)]} & $R_I = 0.0450$, $wR_2 = 0.0875$ \\
\textbf{Rindices (all data)} & $R_I = 0.0677$, $wR_2 = 0.0937$ \\
\textbf{Largest difference in peak and hole (e Å$^3$)} & 1.242 and $-1.000$ \\
\hline
\end{tabular}
\caption{Crystallographic data for (cyclam)Co[[(μ-Cl)U(Me$_2$Pz)$_4$]$_2$·4CH$_2$Cl$_2$}
\end{table}
data for the ZnU\textsubscript{2} cluster, illustrated in Figure 3.2, demonstrates the decaying effect in $\chi^M T$ with decreasing temperature resulting from the influence of a combination of these factors on the spin of the U\textsuperscript{IV} centers. These deviations from spin only behavior significantly hinder the observation of magnetic exchange coupling between an actinide metal and another metal. While it is not feasible to distinguish between spin-orbit coupling effects and ligand field effects solely through the magnetic properties, we can devise two models to correct for the observed loss of magnetic moment. The first takes into account that at low temperatures, the strong spin-orbit coupling in U\textsuperscript{IV} dominates the magnetism. As described in quantitative detail below, our strategy is to subtract out all contributions from U\textsuperscript{IV} leaving only the transition metal spin and residual exchange coupling. In this way, we isolate the magnetism of the actinide from the transition metal, and fit the data by adding back an imposed spin-only value for U\textsuperscript{IV}. In our second model, we treat the actinide and transition metal together by empirically factoring the data to account for both the effects of exchange coupling mediated through U–Cl covalency and spin-orbit coupling inherent to U\textsuperscript{IV}. We consider that as the temperature drops, the observed moment of MU\textsubscript{2} complexes immediately drops, even for ZnU\textsubscript{2}, which should behave as a system containing isolated U\textsuperscript{IV} spins. It is important to note that at room temperature, ZnU\textsubscript{2} does display spin-only behavior such that our reduction factor is physically meaningful. The factored data corrects for spin-orbit coupling and ligand field effects, such that any deviation from the spin-only value for any given cluster is due to exchange coupling of the magnetic ions that comprise the cluster. In this way, we estimate upper and lower bounds for the exchange energy between the spins on both uranium(IV) centers and the transition metal.

The temperature-dependent magnetic susceptibility data for CoU\textsubscript{2} and ZnU\textsubscript{2} display qualitatively similar trends and are dominated by a reduction in the effective spin of the 5f\textsuperscript{2} configuration of U\textsuperscript{IV} as the temperature decreases (see Figure 3.2). We note that at room temperature, ZnU\textsubscript{2} does display spin-only behavior such that our reduction factor is physically meaningful. The factored data corrects for spin-orbit coupling and ligand field effects, such that any deviation from the spin-only value for any given cluster is due to exchange coupling of the magnetic ions that comprise the cluster. In this way, we estimate upper and lower bounds for the exchange energy between the spins on both uranium(IV) centers and the transition metal.

**Table 2.** Selected Interatomic Distances (Å) and Angles (º) Observed for (cyclam)M[([μ-
Cl]U(Me\textsubscript{2}Pz)\textsubscript{4}]\textsubscript{2}. (MU\textsubscript{2}; M = Co, Ni, Cu, Zn).

<table>
<thead>
<tr>
<th></th>
<th>CoU\textsubscript{2}</th>
<th>NiU\textsubscript{2}</th>
<th>CuU\textsubscript{2}</th>
<th>ZnU\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(1)-Cl(1)</td>
<td>2.800(2)</td>
<td>2.838(2)</td>
<td>2.785(2)</td>
<td>2.822(2)</td>
</tr>
<tr>
<td>M(1)-Cl(1)</td>
<td>2.668(2)</td>
<td>2.564(2)</td>
<td>2.774(2)</td>
<td>2.680(2)</td>
</tr>
<tr>
<td>U(1)-N(1)</td>
<td>2.393(7)</td>
<td>2.375(8)</td>
<td>2.396(6)</td>
<td>2.392(5)</td>
</tr>
<tr>
<td>U(1)-N(2)</td>
<td>2.389(7)</td>
<td>2.388(8)</td>
<td>2.390(6)</td>
<td>2.380(5)</td>
</tr>
<tr>
<td>U(1)-N(3)</td>
<td>2.385(7)</td>
<td>2.397(8)</td>
<td>2.392(6)</td>
<td>2.387(5)</td>
</tr>
<tr>
<td>U(1)-N(4)</td>
<td>2.377(7)</td>
<td>2.400(8)</td>
<td>2.385(5)</td>
<td>2.406(5)</td>
</tr>
<tr>
<td>U(1)-N(5)</td>
<td>2.413(7)</td>
<td>2.401(8)</td>
<td>2.415(6)</td>
<td>2.423(5)</td>
</tr>
<tr>
<td>U(1)-N(6)</td>
<td>2.433(7)</td>
<td>2.419(7)</td>
<td>2.427(6)</td>
<td>2.414(5)</td>
</tr>
<tr>
<td>U(1)-N(7)</td>
<td>2.388(7)</td>
<td>2.386(8)</td>
<td>2.390(6)</td>
<td>2.381(5)</td>
</tr>
<tr>
<td>U(1)-N(8)</td>
<td>2.427(11)</td>
<td>2.389(7)</td>
<td>2.407(6)</td>
<td>2.392(5)</td>
</tr>
<tr>
<td>M(1)-N(9)</td>
<td>1.962(7)</td>
<td>2.059(8)</td>
<td>2.017(6)</td>
<td>2.087(5)</td>
</tr>
<tr>
<td>M(1)-N(10)</td>
<td>1.983(6)</td>
<td>2.063(8)</td>
<td>2.022(5)</td>
<td>2.082(5)</td>
</tr>
<tr>
<td>U(1)-Cl(1)-M(1)</td>
<td>138.76(8)</td>
<td>139.47(9)</td>
<td>137.61(7)</td>
<td>138.31(6)</td>
</tr>
</tbody>
</table>
emu·K/mol for CoU₂, corresponding well with the expectation for two uncoupled U⁴⁺ ions and one low-spin Co⁷⁺ ion. However, as the temperature is lowered, the two compounds display somewhat different behavior, in that the $\chi_M T$ value decays less rapidly for CoU₂. Since the structures are similar (see Table 2), differences in the ligand field about uranium(IV) alone cannot account for this variation in the decay of $\chi_M T$. Rather, this difference suggests the presence of magnetic exchange coupling between the Co⁷⁺ and U⁴⁺ centers in the CoU₂ cluster.

In order to estimate the magnitude of the exchange energy, we can first attempt to extract the component of the magnetic susceptibility due to the Co⁷⁺ center from that of U⁴⁺, and subsequently reinstate an idealized spin-only U⁴⁺ susceptibility. Subtraction of the ZnU₂ data from the CoU₂ data should yield $\chi_M T$ for an isolated $d^7$ Co⁷⁺ ion together with any residual moment due to exchange coupling. The plot of this subtracted data, shown in blue in Figure 3.2, is consistent with an isolated Co⁷⁺ center at high temperature, and corresponds to the observed $\chi_M T$ value of 0.41 emu·K/mol, independently measured for (cyclam)CoCl₂. However, as the temperature drops, $\chi_M T$ begins to rise, reaching a maximum of 0.68 emu·K/mol at 40 K. This elevation of $\chi_M T$ at low temperature is indicative of ferromagnetic exchange between the U⁴⁺ and Co⁷⁺ metal centers. To estimate the strength of the exchange coupling, MAGFIT 3.1² was employed to fit the subtracted magnetic susceptibility data above 70 K (where an inflection point occurs in the data) using a spin Hamiltonian of the form $\hat{H} = -2J \hat{S}_{Co} \cdot (\hat{S}_{U(1)} + \hat{S}_{U(2)}) + g\mu_B \hat{S} \cdot B$.

In order to account for a spin-only ($S=1$) contribution from the two U⁴⁺ centers to the total spin, a temperature-invariant contribution of 2.00 emu·K/mol was added back into the data. Optimization of the fit parameters gave $J = 15$ cm⁻¹, $g = 1.92$, and TIP = $3.16 \times 10^{-4}$ emu/mol.
The adjusted data as well as the optimized fit for the CoU\textsubscript{2} cluster are shown in Figure 3.3 (blue diamonds). Reoptimization of the data for the NiU\textsubscript{2} cluster from our previous work leads to a slight increase in $J$ from 2.3 cm\textsuperscript{-1} to 2.8 cm\textsuperscript{-1} with $g = 1.96$ and $\text{TIP} = 5.15 \times 10^{-4}$ emu/mol (Figure 3.3, red circles). We note that these $J$ values represent only a lower bound on the exchange energy, because the foregoing treatment eliminates the effects of spin-orbital contributions and ligand field effects, but only subsequently accounts for the spin at the U\textsuperscript{IV} centers by adding a constant contribution of 2.00 emu·K/mol for the two U\textsuperscript{IV} centers.

In an effort to provide an upper bound for the exchange energy, we propose a second model in which we assume that the reduction in $\chi_M T$ as temperature is decreased in the ZnU\textsubscript{2} and CoU\textsubscript{2} data sets can be modeled by combining the effects of spin-orbit coupling and ligand field perturbations into a single empirical factor based on the magnetic susceptibility of the ZnU\textsubscript{2} cluster. In ZnU\textsubscript{2}, the deviation of $\chi_M T$ from the spin-only value of 2.00 emu·K/mol is quantified as $\chi_M T = (2.00 \text{ emu·K/mol})/r$, where $r$ is a temperature-dependent empirical parameter that accounts for the spin reduction at the individual U\textsuperscript{IV} centers for the ZnU\textsubscript{2} complex. For example, at 5 K, $\chi_M T$ is 0.104 emu·K/mol, giving a reduction factor, $r$ of 19.183 at this temperature. Since the coordination environment of the U\textsuperscript{IV} centers is the same for the ZnU\textsubscript{2} and CoU\textsubscript{2} clusters, and $r$ only describes spin reduction at U\textsuperscript{IV}, we assume that $r$ as a function of temperature is identical for both compounds. Therefore, we can account for the loss of spin on the individual U\textsuperscript{IV} centers by multiplying the measured $\chi_M T$ data for the CoU\textsubscript{2} cluster by the function $r(T)$ determined for the ZnU\textsubscript{2} cluster. In effect, we have corrected the CoU\textsubscript{2} data for any spin loss at the individual U\textsuperscript{IV} centers, and any deviation from its room-temperature $\chi_M T$ value of 4.375 cm\textsuperscript{-1} is attributed to exchange coupling between U\textsuperscript{IV} and Co\textsuperscript{II}. Fitting this spin-corrected CoU\textsubscript{2} data using the Hamiltonian described above gives $J = 48$ cm\textsuperscript{-1}, $g = 1.80$, and $\text{TIP} = 1.67 \times 10^{-4}$ emu/mol.

Figure 3.3. Empirical $\chi_M T$ data arising upon subtraction of the ZnU\textsubscript{2} cluster data from the CoU\textsubscript{2} (blue diamonds) and NiU\textsubscript{2} (red circles) cluster data. A calculated value of 2.00 emu·K/mol has been added to represent a spin-only contribution from of the U\textsuperscript{IV} centers. Best calculated fits to the data are shown as black lines ($J_{\text{min}}(\text{Co}) = 15 \text{ cm}^{-1}$, $J_{\text{min}}(\text{Ni}) = 2.8 \text{ cm}^{-1}$); see text for details.
This treatment was also applied to the NiU$_2$ data from our previous study to give $J = 19$ cm$^{-1}$, $g = 1.85$, and TIP = $5.15 \times 10^{-4}$ emu/mol (Figure 3.4, red circles).

As in our previous study of NiU$_2$, variable-field magnetization experiments on the CoU$_2$ cluster show a significant separation of the isofield lines at low temperatures, consistent with a large axial anisotropy (see Figure 3.5); however, quantitative methods for fitting these data have yet to produce a reasonable fit. Despite the presence of zero-field splitting, ac magnetic susceptibility measurements performed between 1.8 K and 10 K with oscillating frequencies of up to 1500 Hz did not display any out-of-phase signal indicative of single-molecule magnet behavior.

Figure 3.4. Plots of $\chi_M T$ data for the CoU$_2$ (blue diamonds) and NiU$_2$ (red circles) clusters upon modification to account for the loss of spin of the U$^{IV}$ centers at low temperatures. Calculated fits to the data are shown as black lines ($J_{\text{max}}$(Co) = 48 cm$^{-1}$, $J_{\text{max}}$(Ni) = 19 cm$^{-1}$); see text for details.
3.4 Conclusions

The foregoing results demonstrate the synthesis of a new trinuclear cluster complex, (cyclam)Co[(μ-Cl)U(Me$_2$Pz)$_4$]$_2$, exhibiting ferromagnetic exchange coupling. As previously noted for the analogous NiU$_2$ cluster,$^{6g}$ this ferromagnetic exchange is consistent with a superexchange mechanism in which the spin of the 3d$_z^2$ orbital of the Co$^{II}$ center feeds into the sigma orbital system of the bridging chloride ligands, but is then orthogonal to the 5f$_{xyz}$ and 5f$_{z(x^2-y^2)}$ orbitals of the U$^{IV}$ centers. Two methods for fitting the temperature dependence of the magnetic susceptibility data for the cluster—one that treats the uranium and transition-metal contributions separately, and the other that factors spin-orbit coupling, ligand field effects, and exchange coupling into a single empirical factor—enabled estimation of upper and lower bounds for the exchange energy, suggesting $15 \text{ cm}^{-1} < J < 48 \text{ cm}^{-1}$. Importantly, this represents significantly stronger magnetic exchange coupling than typically encountered for lanthanide-containing cluster systems.$^4$ Thus, the idea that relatively strong magnetic exchange coupling might be realizable by taking advantage of the enhanced radial extension of 5f orbitals of actinide elements appears to be valid. This bodes well for future work attempting to utilize actinide elements in the generation of new single-molecule magnets.

3.5 Acknowledgements

This research was funded by NSF Grant No. CHE-0617063. We thank the UC President’s Postdoctoral Fellowship Program for support of B.M.B. and Drs. Frederick J. Hollander and Allen G. Oliver for expert advice on crystal structure determinations.

**Figure 3.5.** A plot of reduced magnetization, $M / N \mu_B$ (where $N$ is Avogadro’s number and $\mu_B$ is the Bohr magneton) versus $H / T$ for (cyclam)Co[(μ-Cl)U(Me$_2$Pz)$_4$]$_2$. Data were measured from 1.8 to 10 K at the seven field strengths specified.
3.6 References and Notes


Chapter 4: Tetranuclear Uranium Clusters via Reductive Cleavage of 3,5-Dimethylpyrazolate

4.1 Introduction

Actinide metal centers are of fundamental interest for possessing electronic structures that are distinct from those of transition metals and lanthanides. However, the combination of increased spin-orbit coupling relative to transition metals and enhanced ligand field effects relative to lanthanides renders modeling the magnetic behavior of actinide-containing molecules particularly challenging. Such factors have a related impact on the chemical reactivity of actinide elements, which has prompted a revival of interest in the coordination chemistry and small-molecule reactivity of uranium. Among the intriguing reactivity patterns uncovered of late are transformations for which transition metal and lanthanide analogues had not previously been identified, as well as some transformations common for transition metal or lanthanide systems, but previously thought to be impossible for actinides.

Chapters 2 and 3 focused on the reactivity of tetravalent uranium with 3,5-dimethylpyrazolate (Me$_2$Pz$^-$) to form the homoleptic dimer, [U(Me$_2$Pz)$_4$]$_2$. Significantly, this reactivity was found to extend to the terminal chloride ligands of certain late transition metal complexes, enabling isolation of a series of linear chloride-bridged clusters of formula (cyclam)M[µ-Cl]U(Me$_2$Pz)$_4$]$_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; M = Co, Ni, Cu, Zn). The isostructural nature of this series facilitated a partial deconvolution of the magnetic susceptibility data, revealing the presence of ferromagnetic exchange interactions in the Co(II)- and Ni(II)-centered clusters. In an effort to increase the strength of the exchange coupling within such species, we undertook investigations intended to produce analogues incorporating uranium(III) in place of uranium(IV). Herein, we report the unanticipated ability of uranium(III) to reductively cleave Me$_2$Pz$^-$, leading to a remarkable series of tetranuclear clusters.
incorporating the new 4-ketimidopent-2-ene-2-imido (kipi3–) ligand (see Eq 1).

\[
\text{3,5-dimethylpyrazolato (Me2Pz)} \quad + \quad 2e^- 
\rightarrow 
\text{4-ketimidopent-2-ene-2-imido (kipi3–)}
\]

(1)

The kipi3– ligand represents an exotic latecomer to the acetylacetonato (acac–) ligand family. Unlike the related and widely-utilized β-diketimido (nacnac–) ligands,5 kipi3– can be represented as containing both imido and ketimido functionalities. Thus, it provides a true nitrogen-based, isoelectronic analogue of acac–, a ligand that has played a long and vital role in coordination chemistry. The activation of Me2Pz– to form kipi3– is unprecedented, both in f-element and transition metal chemistry, but is now found to provide the basis for the formation of three new tetranuclear uranium clusters: (Me2Pz)10U4(kipi)2 (1), (Me2Pz)8U4(kipi)2 (2), and (Me2Pz)11U4(kipi) (3). As outlined in Scheme 1, each cluster can be obtained from a reaction between UI3(THF)4 and KMe2Pz, with the isolation of pure crystalline forms relying upon differences in solubilities and crystallization rates.6

4.2 Experimental

**General Considerations.** The syntheses and manipulations of the extremely air and moisture sensitive compounds described below were conducted under nitrogen with rigorous exclusion of air and water using Schlenk and glovebox techniques. The glovebox used was a Vacuum Atmospheres Nexus One employing an Engelhard Corp. Q-5 catalyst. Tetrahydrofuran was distilled over sodium and benzophenone. Toluene and diethyl ether were saturated with N2, passed through an activated alumina column, degassed by three freeze-pump-thaw cycles, and stored under N2 over 3 Å molecular sieves. The solvent C6D6 (Cambridge Isotope Laboratories) was distilled over NaK alloy and benzophenone and degassed by three freeze-pump-thaw cycles. The compounds UI315 and KMe2Pz3 were synthesized as previously described. NMR experiments were performed at the University of California, Berkeley on a Perkin Elmer 2400 Series II combustion analyzer.

**Crystallography.** Crystals were mounted on Kapton loops and transferred to a Brüker APEX diffractometer and cooled in a nitrogen stream. The SMART program package was used to determine the unit cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). Data integration was performed by SAINT and the absorption correction provided by SADABS. Subsequent calculations were carried out using the SHELXTL program. The structures were solved by direct methods and refined against \(F^2\) by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

1: brown crystals, triclinic, \(P\overline{1}\) (no. 2), \(a = 10.988(7)\) Å, \(b = 12.829(8)\) Å, \(c = 13.180(8)\) Å, \(\alpha = 104.500(9)^\circ\), \(\beta = 97.385(9)^\circ\), \(\gamma = 102.312(8)^\circ\), \(V = 1724.6(19)\) Å³, \(Z = 1\), \(R1 = 0.0662\) (\(I > 2\sigma(I)\)), \(wR2 = 0.1537\) (all data), 4783 symmetry independent reflections, 397 parameters, 0 restraints.
2: dark purple crystals, tetragonal, \(P\overline{4}2_1c\) (no. 114), \(a = 14.978(2)\ \text{Å}, \ c = 14.978(2)\ \text{Å}, \ V = 3174.5(11)\ \text{Å}^3, \ Z = 2, \ R_1 = 0.0428 \ (I > 2\sigma(I)), \ wR_2 = 0.1017 \ (\text{all data}), 2153 \text{ symmetry independent reflections, 80 parameters, 0 restraints.}

3: brown crystals, triclinic, \(P\overline{1}\) (no. 2), \(a = 15.575(4)\ \text{Å}, \ b = 21.993(6)\ \text{Å}, \ c = 22.479(6)\ \text{Å}, \ \alpha = 88.103(3)^\circ, \ \beta = 81.477(4)^\circ, \ \gamma = 77.062(4)^\circ, \ V = 1724.6(19)\ \text{Å}^3, \ Z = 4, \ R_1 = 0.0529 \ (I > 2\sigma(I)), \ wR_2 = 0.1341 \ (\text{all data}), 26914 \text{ symmetry independent reflections, 1585 parameters, 0 restraints.}

CCDC 722750 (1), CCDC 722752 (2), and CCDC 722751 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Electrochemistry.** Cyclic voltammetry was performed in a 0.1 M acetonitrile solution of \((\text{Bu}_4\text{N})\text{PF}_6\) using a Bioanalytical systems CV-50W voltammograph, a platinum disk working electrode, a platinum wire supporting electrode, and a silver wire reference electrode. Reported potentials are all referenced to the \(\text{Cp}_2\text{Fe}^{0/1+}\) couple and were determined using ferrocene as an internal standard.

**Magnetic Measurements.** Powder microcrystalline magnetic samples were prepared in a frozen eicosane matrix and sealed in quartz tubes under vacuum. Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data measurements were performed at temperatures ranging from 5 to 300 K, using applied fields of 0.1, 0.5, and 1 T. Magnetic data were corrected for the diamagnetic contributions from the quartz sample holder and eicosane, as well as for the core diamagnetism of each sample. Core diamagnetism was estimated using Pascal’s constants to give \(\chi_D = -8.9 \times 10^{-4}\ \text{emu/mol for (Me}_2\text{Pz})_8\text{U}_4\text{(kipi)}_2\).

**\((\text{Me}_2\text{Pz})_{10}\text{U}_4\text{(kipi)}_2\) (1) and \((\text{Me}_2\text{Pz})_8\text{U}_4\text{(kipi)}_2\) (2).** Tetrahydrofuran (10 mL) was added to a vial charged with UI\(_3\) (0.682 g, 1.10 mmol). After stirring for 2 h, residual solvent was removed under reduced pressure (10\(^{-3}\) Torr) to give UI\(_3\)(THF)\(_4\). Toluene (10 mL) was added to the deep blue solid, and solid KMe\(_2\text{Pz}\) (0.583 g, 4.34 mmol) was subsequently added with vigorous stirring. Stirring was continued for 24 h and a gray, slightly radioactive precipitate was removed from the brown solution by filtration. Attempts to solubilize and characterize any uranium-containing products from this solid were unsuccessful. The solution was concentrated under reduced pressure for 3 h, affording a brown tar. Toluene was added, and filtration of the resulting solution infrequently yielded sub-milligram quantities of crystalline \((\text{Me}_2\text{Pz})_{10}\text{U}_4\text{(kipi)}_2\) (1), which was analyzed by single crystal x-ray diffraction. Solvent was removed from the filtrate under reduced pressure until the solution reached saturation. Cooling of the saturated solution to –25 °C resulted in the formation of purple hexagonal crystals identified as \((\text{Me}_2\text{Pz})_8\text{U}_4\text{(kipi)}_2\) (2) by single crystal x-ray analysis (30 mg, 5%). \(^1\text{H NMR (C}_6\text{D}_6, 298 K): \delta = -21.8 \ (s, 12H, (N=C)\text{CHMe}_2, \Delta\nu_{\frac{1}{2}} = 7.5 \text{ Hz}), -6.3 \ (s, 4H, \text{Me}_2\text{HC}_3\text{N}_2, \Delta\nu_{\frac{1}{2}} = 1.9 \text{ Hz}), -6.2 \ (s, 4H, \text{Me}_2\text{HC}_3\text{N}_2, \Delta\nu_{\frac{1}{2}} = 5.6 \text{ Hz}), 8.2 \ (s, 4H, \text{Me}_2\text{HC}_3\text{N}_2, \Delta\nu_{\frac{1}{2}} = 3.1 \text{ Hz}), 29.3 \ (s, 4H, \text{Me}_2\text{HC}_3\text{N}_2, \Delta\nu_{\frac{1}{2}} = 2.5 \text{ Hz}) \text{ ppm. Anal. Calcd. for C}_{50}\text{H}_{70}\text{N}_{20}\text{U}_4: C, 31.55; H, 3.71; N, 14.72. Found: C, 31.82; H, 3.70; N, 14.67.**
Tetrahydrofuran (10 mL) was added to a vial charged with UI$_3$ (0.682 g, 1.10 mmol). After stirring for 2 h, residual solvent was removed under reduced pressure (10$^{-3}$ Torr) to give UI$_3$(THF)$_4$. Toluene (10 mL) was added to the deep blue solid, and solid KMe$_2$Pz (0.583 g, 4.34 mmol) was subsequently added with vigorous stirring. Stirring was continued for 24 h and a gray, slightly radioactive precipitate was removed from the brown solution by filtration. Attempts to solubilize and characterize any uranium-containing products from this solid were unsuccessful. The solvent was removed under reduced pressure (10$^{-3}$ Torr) and toluene was added to the brown tar-like product. The solution was filtered and solvent was completely removed from the filtrate to form another dark brown tar. The tar was washed with cold acetonitrile (10 mL), and the product was collected on MAGNA nylon-supported filter paper with 0.22 $\mu$m pores. After drying on the filter paper, the resulting brown powder was washed with cold acetonitrile (3 x 2 mL) to give (Me$_2$Pz)$_{11}$U$_4$(kipi) (3) (110 mg, 19%). Though the acetonitrile washes lower the yield significantly due to the moderate solubility of 3 in acetonitrile, the washes are necessary to obtain pure product. Single crystals of 3 suitable for x-ray analysis were obtained by dissolving the brown powder in a minimal amount of diethyl ether and cooling the saturated solution to –25 °C for two days. $^1$H NMR (CDCl$_3$, 294 K): $\delta$ = 56.8, 51.4, 38.0, 34.1, 30.8, 30.7, 16.3, 14.9, 14.1, 13.9, 11.0, 9.9, 3.4, 1.1, –13.2, –14.2, –16.3, –17.2, –22.8, –31.4, –32.0, –119.2, –123.8, –123.9 ppm. Anal. Calcd. for C$_{60}$H$_{84}$N$_{24}$U$_4$: C, 34.42; H, 4.04; N, 16.06. Found: C, 33.87; H, 3.92; N, 15.40.

4.3 Results and Discussion

Syntheses and Structure of (Me$_2$Pz)$_{10}$U$_4$(kipi)$_2$ (1). Crystals of 1 were isolated after washing the reaction mixture with toluene, following the removal of a grey precipitate by
filtration. The preparation of 1 is less reliable than that of 2 or 3, and consequently our characterization of it is limited to a single crystal x-ray diffraction study. As shown in Figure 4.1, its solid state structure consists of ten Me2Pz⁻ ligands surrounding a core composed of four U⁴⁺ centers and two kipi³⁻ ligands. The U⁴⁺ centers are arranged in a rhomb with four edge-spanning pyrazolate ligands. The two metals at the acute corners of the rhomb each bear two terminal pyrazolates, while those at the obtuse corners are each ligated by just one terminal pyrazolate. The two μ₃:μ₂ bridging kipi³⁻ ligands lie above and below the U₄ plane and are related by inversion symmetry.

| Table 1. Selected Interatomic Distances (Å) in 1, 2, and 3. |
|----------------------------------|-----------------|-----------------|
|                                  | U–Nkipi         | C–Nkipi         | U···Ckipi        |
| (Me₂Pz)₁₀U₄(kipi)₂ (1)           | 2.2182(9)       | 1.3141(7)       | 2.852(1)         |
|                                  | 2.298(1)        | 1.3286(6)       | 2.965(1)         |
|                                  | 2.347(1)        |                 | 3.05(1)          |
|                                  | 2.556(1)        |                 |                 |
|                                  | 2.558(1)        |                 |                 |
| (Me₂Pz)₈U₄(kipi)₂ (2)            | 2.4089(3)       | 1.3560(4)       | 2.6704(3)        |
|                                  | 2.4251(3)       |                 | 2.7092(3)        |
|                                  |                 |                 | 2.7851(4)        |
|                                  |                 |                 | 2.7851(4)        |
| (Me₂Pz)₁₁U₄(kipi)₃ (3)           | 2.2171(5)       | 1.4035(3)       | 2.5859(5)        |
|                                  | 2.2368(4)       | 1.4056(3)       | 2.6082(6)        |
|                                  | 2.2456(4)       | 1.4203(3)       | 2.6153(4)        |
|                                  | 2.2473(5)       | 1.4449(3)       | 2.6209(6)        |
|                                  | 2.3311(5)       |                 | 2.6285(4)        |
|                                  | 2.3348(4)       |                 | 2.6542(5)        |
|                                  | 2.3376(5)       |                 | 2.6751(4)        |
|                                  | 2.3550(4)       |                 | 2.6804(5)        |
|                                  | 2.3557(4)       |                 | 2.6903(5)        |
|                                  | 2.3588(4)       |                 | 2.6983(5)        |
|                                  | 2.3679(6)       |                 | 2.6993(5)        |
|                                  | 2.3896(6)       |                 | 2.7048(4)        |

The geometry and highly-coordinating nature of the kipi³⁻ ligand in 1 are consistent with the changes expected for a formal two-electron reduction of Me₂Pz⁻, resulting in cleavage of the N–N bond (see Eq. 1). Although this is the first instance of a structurally characterized kipi³⁻ unit, precedent for reductive cleavage of N–N bonds in molecules of the type RN=NR by trivalent uranium is well established. Also, nitrogen-based ligand reduction to form multinuclear
uranium clusters has been explored in compounds such as the azido/nitrido U IV chain, \{[Cs(MeCN)₃][U₄(µ-N)(µ-N₃)₈(MeCN)]₈\}, and the molecular ring species, \{(Cs₅Me₅)₂U(µ-N)U(µ-N₃)₈(C₅Me₅)₈\}₄. In the new kipi³⁻ ligand, the pyrazolate backbone is bowed to a C–C–C angle of 127(2)°, while the N···N distance is increased to 2.99(2) Å, well beyond that of the intact Me₂Pz⁻ units in the structure (~1.4 Å). Despite bridging multiple uranium centers, the U–N_{kipi} distances in 1 (see Table 1) are only slightly longer than the terminal U–N_{ketimido} distances of 2.179(6) Å and 2.185(5) Å reported for (Cs₅Me₅)₂U[–N=CPh₂]₄ and the terminal U=N_{imido} distance of 1.952 Å reported for (Cs₅Me₅)₂U=N–Bu₃–C₆H₂. Note that the core of 1 may garner additional stabilization from the short U···C_{kipi} distances, which are comparable to the mean U–C separation in sterically-saturated uranium cyclopentadienyl compounds.

**Syntheses and Structure of (Me₂Pz)₈U₄(kipi)₂ (2).** Further concentration of solutions from which 1 had been isolated led to crystallization of (Me₂Pz)₈U₄(kipi)₂ (2), exhibiting the structure displayed in Figure 4.2. Here, a more compact cubane-type cluster core is observed, consisting of a tetrahedron of uranium atoms with each face capped by a nitrogen atom from one of two opposing kipi³⁻ ligands. Four bridging Me₂Pz⁻ ligands span the equatorial faces of the cubane unit, while the other four Me₂Pz⁻ ligands provide a terminal ligand for each uranium center. The U···C_{kipi} distances are significantly shorter than in 1 due to the coplanarity of the nitrogen atoms of the kipi³⁻ ligand and two of the uranium centers. As opposed to the structure of 1, in which the carbon backbone of each kipi³⁻ ligand is tilted toward a single uranium atom, the carbon atoms of the kipi³⁻ ligands in 2 are equidistant from two uranium atoms. Further, the N–C_{kipi} bonds of 2 are longer than in 1, suggesting more extensive delocalization of the ligand charge within the more compact structure of the cubane cluster core.

In contrast to 1, which contains four U IV ions, the highly-symmetric cubane cluster (Me₂Pz)₈U₄(kipi)₂ (2) is mixed valent. With eight Me₂Pz⁻ and three kipi³⁻ anions, it formally contains two U III centers and two U IV centers. Such mixed valency has a growing number of examples in molecular uranium cluster chemistry. Compound 2 is unusual in that the majority

![Figure 4.2. Structure of 2, with the [U₄(kipi)₂]⁸⁺ core unit emphasized. Orange, blue, and grey spheres represent U, N, and C atoms, respectively; H atoms are omitted for clarity. The cluster resides on a ̅4 site in the crystal, imparting it with rigorous D₂₀₅ symmetry.](image-url)
of these mixed-valent uranium clusters exhibit structures with a different coordination geometry associated with the differing uranium oxidation states, whereas the crystallographic symmetry of the cubane cluster enforces equivalent coordination environments about each of its four uranium atoms. Such equivalent ligand fields with mixed oxidation states suggest the possibility of electron delocalization. The $^1$H NMR spectrum at 298 K offers evidence for the solution equivalence of the four uranium sites on the NMR timescale, since the Me$_2$Pz-(CH$_3$) peaks correspond to the same symmetry observed in the solid state structure. Thus, the possibility of magnetic double exchange between the U$^{III}$ and U$^{IV}$ centers in 2 exists, although the small quantities of the compound available to date has thwarted our attempts at probing this via magnetic susceptibility measurements.

**Syntheses and Structure of (Me$_2$Pz)$_{11}$U$_4$(kipi) (3).** Removal of the toluene solvent enabled isolation of an additional cluster from the solution that provided compound 2. The resulting black residue was washed with cold acetonitrile to afford (Me$_2$Pz)$_{11}$U$_4$(kipi) (3) as a brown solid. As depicted in Figure 4.3, this cluster is similar to 1 and 2 in that it too features a kipi$^{3-}$ ligand formed via reductive cleavage of an N–N bond of a Me$_2$Pz$^-$ ligand. However, the structure of 3 is unique in that one core kipi$^{3-}$ ligand has been replaced by a bridging $\mu^3:\mu^3$-Me$_2$Pz$^-$ ligand, which to the best of our knowledge represents a new bonding mode for pyrazolates.$^{14}$ Intriguingly, the [U$_4$(kipi)(Me$_2$Pz)]$^{10+}$ cluster core of 3, which also formally contains two U$^{III}$ and two U$^{IV}$ centers, is related to the [U$_4$(kipi)$_2$]$^{8+}$ core of 2 through a two-electron reduction of the $\mu^3:\mu^3$-Me$_2$Pz$^-$ ligand to give a second kipi$^{3-}$ ligand. In the structure of 3, the uranium atoms that make two bonds to the kipi$^{3-}$ ligand each have one terminal pyrazolate ligand, while the uranium atoms with only one bond to the kipi$^{3-}$ ligand each coordinate two terminal pyrazolates. This is probably a steric effect due to the larger space requirements of kipi$^{3-}$ compared to the Me$_2$Pz$^-$ ligand, but also likely reflects the two different oxidation states of uranium. Thus, unlike 2, the structure of 3 is not consistent with the possibility of electron delocalization.

Remarkably, the clusters in 1 and 3 are structural isomers. Transformation of 3 into 1
would entail transfer of two electrons, one from each U$_{III}$ center, to the $\mu^3:\mu^3$-Me$_2$Pz$^-$ ligand, leading to cleavage of its N–N bond and a rearrangement of the core structure involving loss of two U–N$_{kipi}$ bonds and planarization of the four uranium atoms. Attempts to use heat or redissolution in toluene to convert 3 into 1 were unsuccessful, indicating that 3 is the more stable isomer under the conditions tested, even though structurally it seems a very reasonable intermediate in the reaction between UI$_3$ and KMe$_2$Pz to form 1.

Cyclic Voltammetry and Magnetic Susceptibility of (Me$_2$Pz)$_{11}$U$_4$(kipi) (3). Of the three cluster compounds, 3 could be obtained most reliably and in the highest yields. A number of characterization methods were therefore used to probe this species (see Supporting Information). The complicated nature of its $^1$H NMR spectrum suggests that the $C_1$ symmetry of the cluster in the solid state is maintained in solution, although the peaks could not be accurately integrated in this case. Cyclic voltammetry was performed on 3 to probe whether the mixed-valence cluster could be readily reduced or oxidized (Figure 4.4). In acetonitrile solution with 0.1 M Bu$_4$N(PF$_6$)$_2$ as the supporting electrolyte, an irreversible reduction wave was observed at ca. –2 V vs. Cp$_2$Fe$^{0/1+}$. However, this cannot be unambiguously assigned to a U$_{IV/III}$ conversion due to the possibility of Me$_2$Pz$^-$ ligand reduction. In addition, an irreversible oxidation occurs at approximately 0.06 V vs. Cp$_2$Fe$^{0/1+}$. Here it is similarly unclear whether the redox change involves a U$_{III/IV}$ process or oxidation of the kipi$^{3-}$ ligand. Unfortunately, efforts to isolate a clean product from chemical oxidations were unsuccessful.

Variable-temperature magnetic susceptibility data were collected for 3 from 5 to 300 K under a dc field of 0.5 T (Figure 4.5). The data show an almost linear decrease in $\chi_M T$ with decreasing temperature down to ca. 150 K where the drop becomes more severe, eventually reaching 0.30 cm$^3$K/mol at 5 K. With the convoluting effects of temperature independent magnetism, crystal field splitting, and spin-orbit coupling it is difficult to draw any conclusions about the presence of magnetic coupling in this system.$^1$ Since the moment falls well below the level expected for a ground state featuring two independent U$_{III}$ centers, antiferromagnetic
coupling may be present between these two atoms of the mixed-valence cluster. However, confidence in this assessment would require a more complete understanding of how the crystal field splits the spin-orbit coupled ground state of each uranium ion and the extent of orbital angular momentum quenching due to covalency between uranium and the kipi$^{3-}$ ligand.

4.4 Conclusions.

The foregoing results demonstrate the use of uranium(III) in the reductive cleavage of the N–N bond in Me$_2$Pz$^-$ to form an unprecedented 4-ketimidopent-2-ene-2-imido (kipi$^{3-}$) ligand, as

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**Figure 4.5.** Variable-temperature magnetic susceptibility data for 3 in $\chi_M T$ vs. $T$ (a), $\chi$ vs. $T$ (b), and $1/\chi$ vs. $T$ (c) formats.
found integrated within three related tetranuclear uranium clusters. It is possible that such chemistry can extend to other actinides, as well as to highly reducing lanthanide and transition metal systems, potentially providing access to a broad family of kipi3-based cluster molecules. Of particular interest for the present uranium system are efforts to improve upon the synthesis of the mixed-valence cubane cluster 2, and experiments aimed at probing electron delocalization within its highly-symmetric core structure.

4.5 Acknowledgements

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4.6 References and Notes


Chapter 5: Slow Magnetic Relaxation in a Trigonal Prismatic Uranium(III) Complex

5.1 Introduction

The previous chapters have focused on linking uranium to other spin carriers to form exchange coupled multinuclear clusters. While such systems have resulted in the discovery of nearly every transition metal single-molecule magnet, a class of single-molecule magnets has emerged in which the molecule contains just a single paramagnetic metal ion. For five years after the discovery of mononuclear single-molecule magnetism, the only examples of such species were the lanthanide ion complexes $[\text{LnPc}_2]^{n+}$ ($\text{Ln}^{\text{III}} = \text{Tb, Dy, Ho}$; $\text{H}_2\text{Pc} = \text{phthalocyanine}$; $n = -1, 0, 1$). However, recent years have seen an explosion of such compounds incorporating lanthanides, actinides, and some highly anisotropic transition elements. As described in Chapter 1, theoretical and experimental studies have shown that the zero-field splitting responsible for the relaxation barrier is due to removal of the $2J+1$-fold degeneracy of the spin-orbit coupled ground state by the crystal field. In order to observe slow relaxation in such a situation, the lowest level of the ground state manifold must have a highly anisotropic angular momentum and be well

Figure 5.1. Structure of the trigonal prismatic complex $\text{U(Ph}_2\text{BPz}_2)_3$ (1) viewed parallel (top) and perpendicular (bottom) to the pseudo-3-fold rotation axis. Orange, purple, gray, and blue spheres represent U, B, C, and N atoms, respectively; H atoms are omitted for clarity. The coordination at the U$^{\text{III}}$ center approximates $D_{3h}$ symmetry, with U-N distances of 2.487(7)-2.568(7) Å and N-U-N angles of 73.2(2)-73.6(3)° and 83.0(2)-95.1(2)°. The intramolecular U-U distance is 10.791(2) Å.
separated in energy from excited levels. We have been pursuing the possibility that actinide ions, by virtue of their greater spin-orbit coupling and enhanced covalency relative to lanthanides, might be of utility in generating new single-molecule magnets.\(^3\) Herein, we show that a simple trigonal prismatic uranium(III) complex can indeed display slow magnetic relaxation.

### 5.2 Results and Discussion

In searching for this effect, we recognized that, like \(4f^8\) Tb\(^{III}\) and \(4f^9\) Dy\(^{III}\) ions, the \(5f^3\) configuration of U\(^{III}\) can deliver an oblate single-ion anisotropy.\(^4\) For an axial ligand environment, strong spin-orbit coupling can then cause the spin to align preferentially along the unique molecular axis. This minimizes the crystal field energy by reducing contacts between the equatorial f-element charge cloud and the ligand donor atom charges. Deviations from axial spin orientation will result in an increased crystal field energy and a barrier to spin inversion. As an initial test of this hypothesis, we probed the magnetic behavior of the eight-fold symmetric complex \([\text{U(COT)}_2]^–\) (COT\(^2–\) = 1,3,5,7-cyclooctatetraene) at low temperature. Ac magnetic susceptibility measurements performed on K[\text{U(COT)}_2], however, indicated only a very small relaxation barrier, perhaps owing to a lowering of symmetry caused by interactions between the K\(^+\) cations and the complex. We therefore turned our attention to the neutral diphenylbispyrazolylborate complex U\((\text{Ph}_2\text{BPz})_2\)_3 (I), featuring the trigonal prismatic geometry.
depicted in Figure 5.1.\textsuperscript{5} 

Ac magnetic susceptibility data were collected on powder samples of 1 embedded in a frozen hexane matrix. The temperature dependence of the in-phase ($\chi'M$) and out-of-phase ($\chi''M$) ac susceptibility under zero applied dc field is shown at the top of Figure 5.2. The $\chi''M$ signal displays frequency-dependent peaks characteristic of slow magnetic relaxation in discrete molecules. As previously observed for lanthanide systems,\textsuperscript{4a,6} $\chi''M$ represents only a small component of the total susceptibility under zero field. However, as exemplified at the bottom of Figure 5.2, application of a small dc magnetic field can change the relaxation dynamics and drastically increase the $\chi''M$ to $\chi'M$ ratio. The possibility that the ac magnetic susceptibility behavior is due to a small sample impurity is ruled out by the correspondence between $\chi'M$ at low frequency and the dc magnetic susceptibility behavior (Figure 5.3).

In order to obtain quantitative information regarding the spin relaxation barrier of 1, the frequency dependence of $\chi'M$ and $\chi''M$ at fixed temperatures was examined. Cole-Cole plots were used to fit $\chi'M$ and $\chi''M$ and derive relaxation rates.\textsuperscript{7} Figure 5.4 shows the Arrhenius plots obtained under applied dc fields of 0, 100, and 1000 Oe. From these data, it is evident that the Arrhenius fit describes a thermally-activated pathway independent of the small applied dc fields. Values extracted from the linear region of the plot give an effective relaxation barrier of $U_{\text{eff}} = 20$ cm\textsuperscript{-1} and $\tau_0 = 1 \times 10^{-9}$ s, and are consistent with single-molecule magnet behavior. Previous studies of LnPc\textsubscript{2} complexes suggest that the slow relaxation in such species occurs via an Orbach-type process, whereby phonon energy is transferred to the spin system via the spin-orbit interaction.\textsuperscript{4b} However, the energy level structure for actinide-based molecules may differ considerably due to increased mixing of low-lying states. Further experimental and theoretical work is needed to determine the specific states comprising the thermal activation barrier in 1.

Although the three sets of relaxation data shown in Figure 5.4 follow the same line at
high temperatures, the temperature at which they deviate from linearity is dc field dependent. The deviation from linearity at low temperature can be used to describe the onset of a regime where quantum tunneling of the magnetization is the dominant process.\textsuperscript{1c} We were interested in further studying this aspect of the behavior of 1 since Kramers ions have been shown to display quantum tunneling between opposite orientations of the ground state spin due to mixing of the levels by transverse components of internal magnetic fields.\textsuperscript{8} Such tunneling is maximized at zero applied magnetic field, due to the near degeneracy of the levels. To test whether this is occurring in 1, variable-frequency ac susceptibility data at a number of applied dc fields in the range 0-500 Oe were collected. All data were acquired at 1.8 K, where the deviations from Arrhenius behavior suggest that quantum tunneling is the dominant process (see Figure 5.5). Hindrance of the tunneling should decrease the characteristic frequency as the frequency moves closer to the Arrhenius line. If quantum tunneling of the magnetization due to the Kramers ground state is present at 1.8 K, a significant drop should occur in the resonant frequency. Figure 5.5 shows a plot of the resonant frequencies at a number of applied dc fields between 0 and 500 Oe. As predicted, a significant dip in frequency is observed, reaching a minimum in the tunneling rate (corresponding to a maximum in the relaxation time) at an applied field between 75 and 100 Oe. This result is consistent with Figure 5.4, where the relaxation rate at 100 Oe applied dc field shows the least deviation from Arrhenius-type behavior.

The observed behavior is indicative of ground state tunneling, yet the mechanism remains uncertain. In many systems, the tunneling can be attributed to intermolecular dipole or hyperfine interactions. To test whether the former are responsible for the tunneling, ac susceptibility experiments were performed on a frozen THF solution of 1. These measurements revealed only a small shift in the peak locations compared to the data obtained for the solid sample, which can be accounted for by slight differences between the solid state and solution geometry of 1. Thus, intermolecular interactions are unlikely to be the source of the observed tunneling. Additionally, our samples contain greater than 99% U-238 (depleted uranium), which has no net nuclear spin, thus eliminating the possibility of a tunneling mechanism stemming from hyperfine interactions.
The foregoing results demonstrate that a simple uranium(III) complex with axial coordination can exhibit single-molecule magnet behavior. It is unlikely that this result is unique, and, given the large spin-orbit coupling and enhanced covalency of actinides relative to lanthanides, there is significant potential for identifying molecules with much larger relaxation barriers. Most importantly, the strategy of maximizing ligand field contributions above and below the equatorial plane in various axial coordination geometries may provide a rational path toward this goal.

5.3 Experimental

Magnetic Measurements. Samples of \( \text{U(Ph}_2\text{BPz}_2)_3 \) (1) were prepared by adding approximately 100 mg of crystalline powder sample compound to a 7 mm quartz tube. Sufficient hexane to cover the sample was added to the quartz tube so that when frozen the matrix would prevent crystallite torquing at high magnetic fields and provide good thermal contact between the sample and the bath. The tube was fitted with a Teflon sealable adapter, evacuated on a Schenck line over three freeze-pump-thaw cycles, and flame sealed under vacuum.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data measurements were performed at temperatures ranging from 1.8 to 301 K, using an applied field of 1 T. Ac magnetic susceptibility data measurements were performed using a 4 Oe switching field. All data for 1 were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal’s constants to give \( \chi_D = -0.00044528 \) emu/mol.

Cole-Cole plots were fitted using formulae describing \( \chi’ \) and \( \chi” \) in terms of frequency, constant temperature susceptibility (\( \chi_T \)), adiabatic susceptibility (\( \chi_S \)), relaxation time (\( \tau \)), and a

![Figure 5.5. Dependence of the magnetic relaxation time for 1 on applied dc field strength at 1.8](image-url)
variable representing the distribution of relaxation times ($\alpha$). All data fitted to $\alpha$ values of $\leq 0.2$ indicating the predominance of a single relaxation process.

5.4 Acknowledgement

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5.5 References and Notes


(7) This material is available free of charge via the Internet at http://pubs.acs.org.


Chapter 6: Observation of a Secondary Slow Relaxation Process for the Field-Induced Single-Molecule Magnet U(H$_2$BPz$_2$)$_3$

6.1 Introduction

The field of single-molecule magnetism,\(^1\) once dominated by the search for strongly-coupled transition metal clusters with a high-spin, high-anisotropy ground state, has diversified as our understanding of the factors governing slow magnetic relaxation in molecules grows. One approach gaining in prominence is the study of single-ion molecular magnets, wherein magnetic anisotropy generated from the interaction between a single metal ion and its ligand field creates a strong preferential orientation of the magnetic moment. This type of molecular magnetism, which arises from a large unquenched orbital moment, was first recognized in lanthanide-based systems, including [LnPc$_2$]$^{n+}$ (Ln$^{III}$ = Tb, Dy, Ho; H$_2$Pc = phthalocyanine; $n = -1, 0, 1$),\(^2\) [Ln(W$_5$O$_{18}$)$_2$]$^{9-}$ (Ln$^{III}$ = Ho, Er), and [Ln(β$_2$-SiW$_{11}$O$_{39}$)$_2$]$^{13-}$ (Ln$^{III}$ = Dy, Ho, Er, Yb),\(^3\) but has recently been extended to the trigonal pyramidal transition metal complex [(tpa$_{Mes}$)$_2$Fe]$^{−}$ (H$_3$tpa$_{Mes}$ = trimesityltris(pyrrolylmethyl)amine)\(^4\) and the trigonal prismatic actinide complex U(Ph$_2$BPz)$_3$\(^5\),. Such compounds further the prospects for single-molecule magnets, potentially bringing the goals of molecule-based information storage, quantum computing, and spin-based electronics closer to reality.\(^7\)

Additional mechanisms for magnetic relaxation can arise in single-ion molecular magnets that are not typically apparent for multinuclear clusters. In particular, the strong spin-orbit coupling and generally lower spin can facilitate phonon-based relaxation mechanisms involving only the ground state (direct relaxation) or the ground state and some real or virtual excited state

![Figure 6.1](image-url). Side (left) and top (right) views of the crystal structure of the trigonal prismatic complex U(H$_2$BPz)$_3$ (1). Orange, purple, gray, and blue spheres represent U, B, C, and N atoms, respectively; H atoms are omitted for clarity except for those bound to B atoms in the depiction at the right. The molecule has approximate $C_{3h}$ symmetry, with U-N distances of 2.4983(4)-2.5754(5) Å, calculated U···H distances of 2.8321(6)-2.9010(6) Å, and N-U-N angles of 77.192(7)-80.208(8)$°$ and 80.444(8)-88.395(8)$°$. The shortest intermolecular U···U separation in the structure is 8.167(2) Å.
(Orbach and Raman relaxation, respectively). The detailed characterization of such processes is of utmost importance, since a gain in knowledge may enable the magnetic relaxation times to be manipulated through simple alterations of the ligand field. To date, however, no compound has been shown to exhibit more than one well-resolved pathway for slow magnetic relaxation at a given temperature. Herein, we demonstrate that the dihydrobispizolylborate complex U(H₂BPz₂)₃ (1) displays multiple relaxation pathways, including an extremely slow relaxation process that becomes dominant at low temperature under an applied magnetic field.

6.2 Results and Discussion

Compound 1 was crystallized from a saturated solution in a mixture of hexanes and toluene. X-ray analysis of a single crystal revealed a trigonal prismatic coordination of the U³⁺ center by the pyrazolate nitrogen atoms (Figure 6.1), similar to that observed previously for U(Ph₂BPz₂)₃. Although the locations of the H atoms are not precisely determined, the calculated positions are in agreement with the results of a previous analysis in which the B-H stretching modes in the infrared spectrum were taken to be consistent with U···H interactions at the lateral faces of the trigonal prism. Such an arrangement accounts for the increased axial elongation of the trigonal prism in the crystal structure of 1 compared with that of U(Ph₂BPz₂)₃.

By the simple electrostatic model discussed in Chapter 1, this axial elongation should lead to a decreased splitting of the 2J+1-fold degeneracy of the spin-orbit coupled ground state by the crystal field, and consequently a smaller relaxation barrier. However, the generality of such effects are as yet poorly understood, especially for actinide complexes where this simple electrostatic model may be perturbed by covalency in the interactions with the ligands.

To compare the spin relaxation behavior of 1 to that of U(Ph₂BPz₂)₃, the frequency

![Figure 6.2](Image)

**Figure 6.2**. Arrhenius plot for 1 in the presence of applied dc fields of 100 and 5000 Oe. Relaxation domains A and B refer to the high frequency and low frequency relaxation processes, as described in the text. The solid line represents a fit to the linear range of frequency region A at 100 Oe.

![Figure 6.3](Image)

**Figure 6.3**. Cole-Cole plots showing the field dependence of multiple relaxation processes occurring in 1 at 1.8 K. Relaxation domains A and B correspond to the ac frequency ranges of 1-1500 and 0.06-1 Hz, respectively. Data in domain A is faded to facilitate visualization. The value of χ)'), at an applied dc field of 5000 Oe is marked with an arrow to indicate its relation to the low-frequency ac susceptibility data.
dependence of $\chi'_M$ and $\chi''_M$ was examined at multiple fixed temperatures. Consistent with a low moment and a smaller relaxation barrier, 1 lacks the zero-field response displayed by U(Ph$_2$BPz$_2$)$_3$. Under an applied dc field of greater than 30 Oe, however, a frequency dependent out-of-phase susceptibility signal is clearly observed, indicating slow magnetic relaxation. Cole-Cole plots were used to fit $\chi'_M$ and $\chi''_M$ in the temperature range 1.8-3.0 K at fields of 100 and 5000 Oe in order to characterize the magnetic relaxation in the frequency range 1-1500 Hz (hereafter referred to as relaxation domain A). From the 100 Oe data in Figure 6.2, the Arrhenius activation barrier to magnetic relaxation for 1 was determined to be 8 cm$^{-1}$, as compared to the barrier of $U_{\text{eff}} = 20$ cm$^{-1}$ observed for U(Ph$_2$BPz$_2$)$_3$. We note, however, that the accuracy of the value for the barrier in 1 is somewhat uncertain, since the relaxation data begin to deviate from Arrhenius behavior at lower temperatures. Additionally, the associated attempt frequency of $\tau_0 = 1.2 \times 10^{-6}$ s is large for a single-molecule magnet, suggesting that the temperature range probed may be intermediate between a high-temperature Arrhenius regime and a low-temperature regime involving relaxation directly between opposite orientations of the magnetic ground state. Increasing the dc field from 100 to 5000 Oe eliminates any strong thermal dependence of the relaxation rate, suggesting that under a 5000 Oe field relaxation does not involve an excited state, as was evident at lower applied fields.

To further investigate the low-temperature relaxation behavior, variable-frequency ac susceptibility data were collected at 1.8 K under a wide range of applied dc fields (Figure 6.3). At each dc field above 500 Oe, two independent relaxation domains were observed: one at high and one at low frequency (hereafter referred to as relaxation domains A and B, respectively). Relaxation domain A roughly includes frequencies from 1-1500 Hz and shows a pronounced asymmetry for the Cole-Cole plot semi-circles. This asymmetry suggests the presence of multiple, closely spaced relaxation processes within relaxation domain A. Owing to their proximity, relaxation times for the individual processes occurring at a given field could not be extracted from the overall curve. Instead, an average of these overlapping relaxation times was calculated by fitting the data to a distribution of relaxation processes using the generalized Debye model. Interestingly, as the dc field is increased, the asymmetry in the Cole-Cole plot disappears and a smooth semicircular arc is observed. We attribute this to the applied field eliminating one of the relaxation processes. The nature of the remaining process in relaxation domain A at 5000 Oe is unclear; however, the lack of thermal dependence (Figure 6.2) and prominence at higher fields suggests a direct process within the ground state Kramers doublet.
Relaxation domain B, shown as unfaded symbols in Figure 6.3, involves extremely low frequencies (0.06-1 Hz). This process operates at the same temperatures and dc fields as the process in domain A; however, its relaxation time is drastically increased, such that it can be characterized by fitting a completely independent Cole-Cole semicircle. Such resolution of multiple processes at a given temperature is, to our knowledge, without precedent in molecular magnetism. The process occurs at a rate that is three orders of magnitude slower than the relaxation pathways operational in domain A, and displays no asymmetry indicative of multiple overlapping processes. Figure 6.4 illustrates the vast difference in relaxation times, as well as the essentially linear increase in the relaxation time for the new process with applied field. The new process displays a weak temperature dependence similar to that observed in the high field data for relaxation domain A (Figure 6.2), but instead of a decrease in relaxation time with increasing dc field, a dramatic and steady increase in relaxation time occurs up to 5000 Oe. This indicates a fundamental difference between the direct relaxation behavior observed in the high-field relaxation domain A data and the as yet unexplained low-frequency process.

6.3 Conclusions

The multiple relaxation processes displayed by U(Ph₂BPz₂)₃ attest to the complexity of the magnetic response in single-ion molecular magnets. Further characterization of this system will require measurements at lower frequencies and temperatures, as well as mapping out the low-lying electronic states to correlate our data with the available relaxation pathways. Analogous experiments performed on other single-ion molecular magnets will reveal whether the behavior observed here is common and might account for the discrepancies between crystal field energy splitting calculations and fits to relaxation barriers. Most critically, the results demonstrate that simply correlating temperature-scanned peak location to relaxation time may conceal a wealth of information about the magnetic relaxation properties of the system, which

![Figure 6.4](image.png)

**Figure 6.4.** Field dependence of the magnetic relaxation time at 1.8 K for processes occurring in relaxation domains A and B.
only a detailed investigation of frequency, dc field, and temperature space can elucidate. Ultimately, obtaining a comprehensive picture of the relaxation pathway manifold may prove essential to efforts aimed at slowing the relaxation dynamics within single-molecule magnets to facilitate their potential applications.

6.4 Experimental

**X-ray Structure Determination.** Dark purple crystals were obtained from a saturated 10:1 hexanes/toluene solution of 1 after 12 h at room temperature. Crystals were mounted on Kapton loops and transferred to a Brüker SMART diffractometer and cooled in a nitrogen stream. The SMART program package was used to determine the unit cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). Data integration was performed by SAINT and the absorption correction provided by SADABS. Subsequent calculations were carried out using the WinGX program. The structures were solved by direct methods and refined against $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Complete crystallographic data is included in the Crystallographic Information File (CIF).

**Magnetic Measurements.** The magnetic sample of U(H$_2$BPz$_2$)$_3$ (1) was prepared by adding 108.9 mg of the crystalline powder compound to a 7 mm quartz tube on top of a layer of eicosane approximately 1 cm high. Sufficient liquid eicosane (at 60 °C) was added to saturate and cover the sample to prevent crystallite torqueing and provide good thermal contact between the sample and the bath. The tube was fitted with a Teflon sealable adapter, evacuated on a Schenk line, and flame sealed under vacuum.

Magnetic susceptibility measurements were collected using a Quantum Design MPMS2 SQUID magnetometer. DC susceptibility data measurements were performed at temperatures ranging from 1.8 to 301 K, using applied fields of 100, 1000, 5000, and 10,000 Oe. Ac magnetic susceptibility data measurements were performed using a 4 Oe switching field. All data for 1 were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal’s constants to give $\chi_D = -0.000259$ emu/mol.

Cole-Cole plots were fitted using formulae describing $\chi'$ and $\chi''$ in terms of frequency, constant temperature susceptibility ($\chi_T$), adiabatic susceptibility ($\chi_S$), relaxation time ($\tau$), and a variable representing the distribution of relaxation times ($\alpha$). All data fitted to $\alpha$ values of $\leq 0.35$.

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6.6 References and Notes

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(12) This material is available free of charge via the Internet at http://pubs.acs.org.